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ABSTRACT

Research on the health effects of oxides of nitrogen and on the role of oxides of nitrogen in producing photochemical smog effects is presented in this report. Prepared by the California State Department of Public Health at the request of the State Legislature, it gives a comprehensive review of available information, as well as the need for air quality and motor vehicle emission standards for oxides of nitrogen. Chapters are titled: The Oxides of Nitrogen and Their Formation, Oxides of Nitrogen from Motor Vehicles, Oxides of Nitrogen from Stationary Sources, Increases in Oxides of Nitrogen Emissions, Oxides of Nitrogen in the Atmosphere, Color Effects of Nitrogen Dioxide in the Atmosphere, Phytotoxicity of Nitrogen Dioxide, Photochemical Effects of Nitrogen Oxides, and Biologic Effects of Nitrogen Dioxide. Summary statements indicate that oxides of nitrogen play an important role in California's air pollution problems. Also, since increases in oxides of nitrogen emissions and nitrogen dioxide concentrations are expected, it is important to consider the direct effects of nitrogen dioxide on health, vegetation, and color of the atmosphere, as well as the photochemical smog effects. Numerous charts, diagrams, and figures are used to support the data. (BL)

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The Oxides of Nitrogen in Air Pollution

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INTRODUCTION

Oxides of nitrogen play an important role in California's air pollution problem. They are essential ingredients in the formation of photochemical air pollution. The complex chain reaction which produces smog manifestations is initiated by the photolysis of nitrogen dioxide. If present in sufficient amounts, nitrogen dioxide is toxic to humans and vegetation. Under some conditions, it imparts a reddish-brown color to the atmosphere.

The State Department of Public Health has continually supported, conducted, and urged others to conduct, research on the health effects of oxides of nitrogen and on the role of oxides of nitrogen in producing the photochemical smog effects. It has retained consultants and has sought the advice of recognized experts on health and other effects and on the smog reaction. It has continually reviewed and evaluated all pertinent information on oxides of nitrogen and has consulted with its Advisory Committee on all developments.

With the establishment of its Vehicle Pollution Laboratory in Los Angeles, the Department has greatly increased its studies of nitrogen oxide emissions from vehicles and of the oxides of nitrogen - hydrocarbon reaction.

In 1964 the State Board of Public Health adopted a resolution stating that, in its opinion, oxides of nitrogen standards for automobile exhaust emissions were needed. As a result, the Board instructed the Department of Public Health to prepare a report on the subject and indicated its intention of considering such standards after reviewing the report.

Later, in June 1965, the State Legislature passed a resolution calling upon the Department to establish standards for oxides of nitrogen as found necessary for the "protection of the public health and well-being". It also directed that a progress report be submitted by the Department in July 1965 to the Senate Fact Finding Committee on Transportation and Public Utilities and the Assembly Interim Committee on Transportation and Commerce; to the Motor Vehicle Pollution Control Board on December 1, 1965; and to the Legislature on or before the fifth day of the 1966 Budget Session.

This report, "The Oxides of Nitrogen in Air Pollution", has been prepared in compliance with these requests. In it is presented a comprehensive review of the available information upon which can be based a sound judgment on the need for air quality and motor vehicle emission standards for oxides of nitrogen.

The report has drawn freely from many sources and includes contributions from several experts. While it gratefully acknowledges all assistance, the Department accepts full responsibility for the interpretation of the data and for the opinions expressed here.

CONCLUSIONS AND RECOMMENDATIONS

Oxides of nitrogen play an important role in California's air pollution and so must be taken into account in any program of setting standards for ambient air quality and motor vehicle emissions. If present in sufficient quantities, nitrogen dioxide can be injurious to health, damage vegetation, and impart an undesirable color to the atmosphere.

Nitrogen oxides are formed during combustion processes. Power plants, internal combustion engines, space heaters, water heaters, and industrial processes comprise the important sources of these gases. The relative contribution of oxides of nitrogen from motor vehicles and non-vehicular sources varies from community to community. In heavily industrialized metropolitan areas, where there are thermal power plants, motor vehicles emit from 50 to 60 percent of the total oxides of nitrogen in the atmosphere. In non-industrialized urban areas, and in the absence of thermal power plants, the contribution from motor vehicles may be as high as 90 percent.

The highest concentrations of oxides of nitrogen (nitric oxide plus nitrogen dioxide) in California have been measured in Los Angeles County. One part per million has been exceeded many times, and the maximum recorded concentration has been 3.9 parts per million. Los Angeles has also had the highest recorded concentrations of nitrogen dioxide in the State, 0.5 part per million having been exceeded many times and 1 part per million having been exceeded on occasion.

Oxides of nitrogen emissions are related to fuel consumption and the number of motor vehicles. These emissions for the State as a whole are expected to almost double by 1980; in the more rapidly growing areas they will more than double. Also, hydrocarbon control may cause an increase in the time-concentration exposure of nitrogen dioxide. The expected increases in oxides of nitrogen emissions and nitrogen dioxide concentrations make it important to consider the direct effects of nitrogen dioxide on health, vegetation, and color of the atmosphere, as well as the photochemical smog effects.

The effects of oxides of nitrogen in air pollution are summarized as follows: These effects, singly or in combination, can be used as the basis for ambient air quality standards.

BIOLOGICAL EFFECTS - The information available on toxicity of nitric oxide indicates that it is less toxic than nitrogen dioxide and that an ambient air quality standard based on the health effects of nitric oxide need not be established at this time. Nitrogen dioxide, however, is more toxic, and its effect on the health of man and animals is of greater concern. Thus, ambient air quality standards for nitrogen dioxide are recommended.

A "serious level" ambient air quality standard for nitrogen dioxide at 3 parts per million for one hour was recommended by the Department's consultants. The concentration of 3 parts per million is not as firmly supported by scientific data as would be desired by the Department and its consultants. It is, however, the best value that can be established at this time. In making their recommendations, the consultants stressed the need of additional research on the health effects of oxides of nitrogen.

The recommended standard is for acute exposures; it does not include considerations for the effect of prolonged exposures to low concentrations. Limited studies have shown that prolonged exposures to nitrogen dioxide at 0.5 - 1.0 part per million can be detrimental to health of animals. However, the data is not considered adequate for establishing a standard based on long-term effects at this time.

PHYTOTOXIC EFFECTS OF NITROGEN DIOXIDE - Data on phytotoxic effects indicate that exposure to 2-3 parts per million of nitrogen dioxide may cause acute damage to sensitive plants. There is also evidence that long-term exposure to NO_2 at concentrations below 1 part per million may lead to growth suppression, chlorosis, and perhaps premature abscission of leaves. Exposures to 1 part per million nitrogen dioxide for eight hours will produce significant growth reduction, expressed as fresh and dry weight, with no visible lesions.

COLORATION EFFECTS - Nitrogen dioxide absorbs light in both the ultraviolet and visible spectrum. In sufficient concentrations it will reduce the brightness and the contrast of distant objects and will impart a yellow-brown color to the horizon sky and distant white objects. The coloration effects are even more noticeable as the number of aerosols in the atmosphere decreases.

It has been estimated that, at 0.25 part per million, on a day when the visibility is 20 miles, the color effect on objects at 10 miles distant will be objectionable to the public.

The concentration of 0.25 part per million nitrogen dioxide is lower than the concentration that would be established in a standard based on phytotoxic effect. It is believed that a standard of 0.25 part per million would prevent possible plant damage by nitrogen dioxide. In addition, the data available indicates that 0.25 part per million is lower than the concentrations at which effects on health would be expected from prolonged exposures to this gas.

PHOTOCHEMICAL SMOG EFFECTS - There is agreement among individuals engaged in photochemical smog studies on the need to control hydrocarbon emissions. With respect to oxides of nitrogen, the studies do not provide a basis for predicting the exact effect of concentrations of these gases to photochemical smog formation. The laboratory studies on photochemical smog show the following:

1. The decision to require hydrocarbon control for motor vehicles is supported by a preponderance of evidence. Control of hydrocarbons alone will reduce eye irritation, vegetation damage, and ozone and aerosol formation; and the greater the degree of hydrocarbon control, the greater the reduction of the smog products. The hydrocarbon control program in California should, therefore, proceed as rapidly as possible.
2. The benefits of further reduction of smog products from oxides of nitrogen control will depend on the effectiveness of the hydrocarbon control program. The more effective the control of hydrocarbons, the less significant will be the benefit realized from the control of oxides of nitrogen. Most of the experimental findings indicate that, with effective hydrocarbon control, moderate reduction of oxides of nitrogen may not further reduce smog effects. In fact, some of the laboratory data indicate that moderate reduction of oxides of nitrogen emissions may negate some of the benefits gained from hydrocarbon control.

In order to achieve clear-cut benefits beyond those from hydrocarbon control, a standard for oxides of nitrogen in the atmosphere would have to be set at a very low level, 0.1 part per million or less. Such a standard would impose a very stringent, perhaps even unrealistic, control of nitrogen oxide emissions from all sources. In view of the uncertainty of the supporting data and the conflicting opinions of scientists, a standard based on the specific role of oxides of nitrogen in photochemical air pollution is not recommended at this time.

Chapter I

THE OXIDES OF NITROGEN AND THEIR FORMATION

The oxides of nitrogen (NO_x) are compounds of the two most abundant gases in air, oxygen and nitrogen. Seven known oxides of nitrogen are shown in Table I:

TABLE I
THE OXIDES OF NITROGEN

Name	Chemical Symbol
Nitrous Oxide	N_2O
Nitric Oxide	NO
Nitrogen Dioxide	NO_2
Nitrogen Trioxide	NO_3
Nitrogen Sesquioxide	N_2O_3
Nitrogen Tetroxide	N_2O_4
Nitrogen Pentoxide	N_2O_5

The first of these, nitrous oxide, is a colorless gas and occurs naturally in air at a concentration of about 0.5 parts per million parts of air by volume (ppm).⁽¹⁾ It is said to be formed by bacterial action and by reaction between nitrogen and atomic oxygen or ozone in the upper atmosphere.⁽²⁾ The gas is employed as an anaesthetic, and its common name is "laughing gas". Chemically it is inert at ordinary temperatures and is of no concern as an air pollutant.

The second, nitric oxide, is formed by the fixation of oxygen and nitrogen at high temperatures according to the reaction $\text{N}_2 + \text{O}_2 = 2\text{NO}$. The burning of petroleum fuels in internal combustion engines and the combustion of natural gas or oil in boilers, furnaces and heaters are important sources of NO in California. Nitric oxide, which is colorless, reacts at ordinary temperatures with the oxygen in air to form the brownish dioxide according to the reaction $\text{NO} + \frac{1}{2}\text{O}_2 = \text{NO}_2$. The coloration effects of nitrogen dioxide is discussed in a subsequent chapter.

The rate of formation of nitrogen dioxide from nitric oxide and oxygen in air increases as the square of the nitric oxide concentration. The reaction proceeds very rapidly at high nitric oxide concentrations and very slowly at low concentrations. At a concentration of 1000 ppm nitric oxide, about 5 minutes are necessary to convert one-half of the nitric oxide to nitrogen dioxide. At a concentration of 1 ppm, 100 hours are required for one-half conversion and, at 0.1 ppm, 1000 hours are required. In the presence of hydrocarbons and when irradiated by sunlight the conversion of nitric oxide to nitrogen dioxide is much faster than can be accounted for by the reaction of nitric oxide with molecular oxygen. The photochemical conversion will be discussed in a later chapter.

The remaining oxides of nitrogen - N_2O_3 , N_2O_4 , NO_3 and N_2O_5 - exist in the atmosphere in equilibrium with nitric oxide, nitrogen dioxide and other compounds, but their concentrations are very small. For example, nitrogen tetroxide exists in equilibrium with NO_2 , i.e., $2 NO_2 \rightleftharpoons N_2O_4$. At a concentration of 0.1 ppm NO_2 in the atmosphere, the equilibrium concentration of N_2O_4 is only 7×10^{-14} ppm.

NO_3 and N_2O_5 in urban air exist in equilibria with ozone (O_3), NO , and NO_2 . It has been calculated that, at concentrations of 0.1 ppm of O_3 and NO_2 and of 0.01 ppm of NO , the upper limit equilibrium concentration of NO_3 is 7.5×10^{-6} ppm. Under the same conditions, the upper limit equilibrium concentration of N_2O_5 is 2.2×10^{-4} ppm. (4)

Thus, of the oxides of nitrogen, only nitric oxide and nitrogen dioxide concentrations are sufficiently high to be of concern in air pollution. Indeterminant mixtures of NO and NO_2 are referred to in this report as NO_x .

Nitrogen dioxide hydrolyzes in water to form nitric and nitrous acid, $2NO_2 + H_2O = HNO_3 + HNO_2$. Chemical methods commonly used to determine the emissions of NO_x from stationary sources or from motor vehicles are based on the measurement of either nitrite (NO_2^-) or the nitrate (NO_3^-) ion. In practice, NO is first oxidized to NO_2 and the latter is then absorbed in an aqueous reagent. The results are usually expressed in terms of NO_2 .

Chemical equilibrium and reaction rate data have indicated that nitric oxide is the predominant oxide of nitrogen formed in combustion processes. Measurements of NO and NO_2 in the exhaust have shown that this is true for internal combustion engines. (5)(6)(7)(8)

The concentration of NO_x emitted from a combustion process is affected by the peak temperature and its duration, the availability of free oxygen and nitrogen, and the rate of cooling of the gases. It has been estimated that at about 2780°F, with 20% oxygen present, 4400 ppm NO is formed at equilibrium and 90% of the equilibrium value is reached in 12 seconds. At 3860°F, 20,000 ppm NO is formed and 90% of the equilibrium concentration is reached in one-half second. (2) To maintain the 90% of the NO formed at the high temperature, however, requires that the gases are cooled to 3140°F in about two-hundredths of a second, or

at a rate of approximately 20,000°C/sec. At temperatures below 2780°F the rate of decomposition of NO to molecular oxygen and nitrogen becomes negligible.⁽²⁾⁽³⁾ However, the amount of NO formed at 2780°F and even at several hundred degrees lower is not negligible from the standpoint of air pollution.⁽²⁾

In the operation of an internal combustion engine, the peak combustion temperature and oxygen content are affected by the air-fuel (A/F) ratio. At A/F ratios below 12:1, the system is oxygen-deficient, and the nitric oxide concentration is found to be very low. Increasing the A/F ratio above 12:1 raises the exhaust NO concentration sharply, reflecting the increase in combustion temperature and the availability of oxygen. The A/F ratio for maximum oxides of nitrogen formation ranges from 15:1 to 17:1, which is slightly leaner than the stoichiometric A/F.⁽⁹⁾ Further leaning of the air-fuel mixture reduces the peak combustion temperature and, thereby, reduces the nitric oxide formation.

The compression ratio, ignition timing, and manifold air pressure also affect the peak combustion temperature. The effects of these factors on oxides of nitrogen concentrations are shown in Figures 1, 2 and 3.⁽⁹⁾ As shown, the effects are greatest when the A/F ratio is about 16:1⁽⁹⁾

The mass emissions of oxides of nitrogen depend on the concentration and on the volume of gases discharged during a combustion process. Thus the modes of motor vehicle operation which produce high temperatures and high exhaust volumes account for the greater part of the mass emissions from automobiles. Way and Fagley⁽¹⁰⁾ found that most of the NO_x emissions from motor vehicles occur during the fast cruise and rapid acceleration modes. Daigh and Deeter⁽¹¹⁾ reported that the quantity of NO_x emitted from motor vehicles increases with vehicle speed. Rose et al, however, reported that exhaust emissions of oxides of nitrogen are independent of average route speed but are dependent on engine air-fuel ratio.⁽¹²⁾

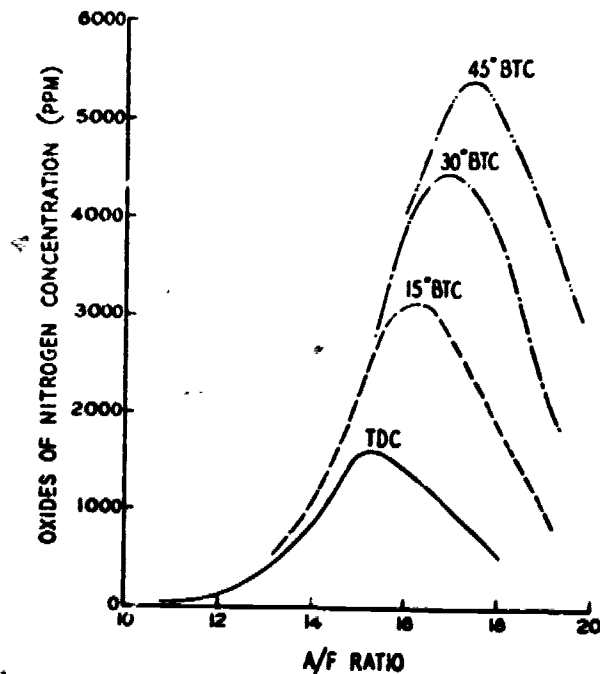
Oxides of nitrogen formation in boilers and other industrial combustion equipment also increases with increasing peak combustion temperatures and to a degree with increasing amounts of excess air provided for combustion. Emissions from power plant boilers have been reduced by recirculating a portion of the flue gases back into the firebox. This reduction was postulated to be the result of a reduction of the temperature of the combustion gases in the zone where nitrogen is fixed.⁽¹³⁾ Reduction of NO_x emissions from steam plants was accomplished by reducing the quantity of primary combustion air in a 2-stage method of combustion. By using 95% primary air and completing the burning with secondary air, NO_x emissions were reduced almost 50%.⁽¹⁴⁾ A decrease in burner load also produced a decrease in flame temperature and a resulting decrease in oxides of nitrogen emissions.⁽¹⁴⁾

In a study of emissions from stationary sources it was found that oxides of nitrogen increased as the heat input to the power of 1.18.⁽¹⁵⁾⁽¹⁶⁾ This exponential increase of oxides of nitrogen may be due to higher combustion temperature attained in the larger combustion equipment.

FIGURE 1

EFFECT OF SPARK TIMING ON OXIDES OF NITROGEN CONCENTRATION

COMPRESSION RATIO 6.7
MANIFOLD AIR PRESSURE 29" Hg
SPEED 1000 RPM

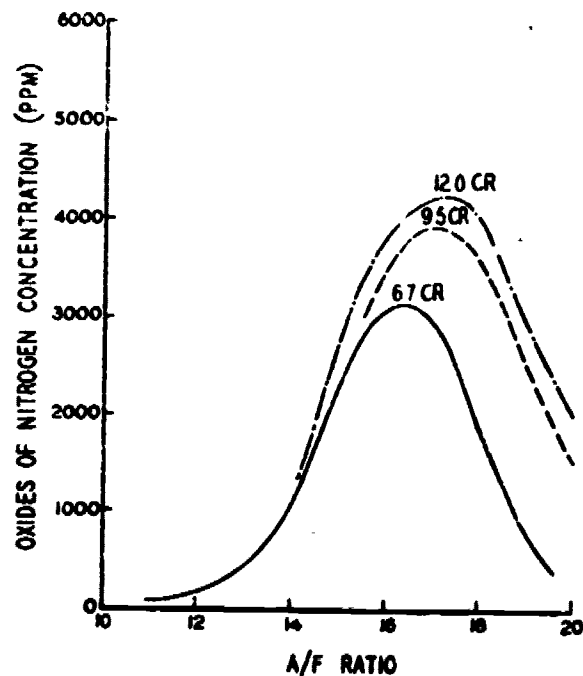


SOURCE: REFERENCE 9

FIGURE 2

EFFECT OF COMPRESSION RATIO ON OXIDES OF NITROGEN CONCENTRATION

MANIFOLD AIR PRESSURE 29" Hg
SPARK 15° BTC
SPEED 1000 RPM

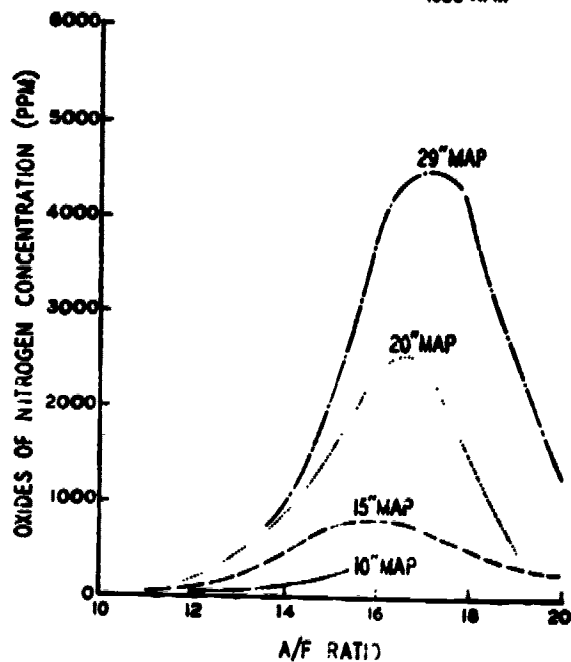


SOURCE: REFERENCE 9

FIGURE 3

EFFECT OF MANIFOLD AIR PRESSURE ON OXIDES OF NITROGEN CONCENTRATION

COMPRESSION RATIO 6.7
SPARK 30° BTC
SPEED 1000 RPM



SOURCE: REFERENCE 9

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Chapter II

OXIDES OF NITROGEN FROM MOTOR VEHICLES

In considering oxides of nitrogen attributable to motor vehicles, it should be noted at the start that the largest percent, almost all in fact, are emitted from the exhaust system. The total of oxides of nitrogen emitted from the crankcase is but one percent of that emitted from the exhaust, according to measurements and theoretical calculations.

Oxides of nitrogen in exhaust emissions have been measured, along with other contaminants, in several surveys. The surveys covered a large number of gasoline vehicles selected to represent either the total vehicle population or special segments of it. These include the Los Angeles Test Station Project, the Coordinating Research Council Survey, and the California Department of Public Health Specialized Vehicle Survey. A brief description and a summary of the data from each of these studies follow:

THE LOS ANGELES TEST STATION PROJECT

The Los Angeles Test Station Project (1962-63) was a cooperative effort of the Auto Club of Southern California, the Automobile Manufacturers Association, the Los Angeles County Air Pollution Control District, the U.S. Public Health Service, the California Motor Vehicle Pollution Control Board, and the State Department of Public Health. It consisted of two parts. Part I - the Correlation Study - determined the relationships of a variety of operating factors to exhaust contaminant concentrations. Part II - the Mass Testing Study - determined the exhaust emissions from more than 1000 cars, using an 8-mode chassis dynamometer cycle. The operating modes and the weighting factors are shown below.

8-MODE CYCLE

<u>Mode</u>	<u>Weighting Factor</u>
0-25 mph acceleration	24.4%
30 mph cruise	6.1
30-15 mph deceleration	6.2
15 mph cruise	5.0
15-30 mph acceleration	45.5
50 mph cruise	5.7
50-20 mph deceleration	2.9
Idle	4.2

In the Correlation Study, NO_x emissions from 28 cars, 17 standard size and 11 compacts, were determined with the following four procedures:

- 1a - Cars were driven in Los Angeles on a route typifying Los Angeles driving. Composite samples were collected using a proportional sampler.
- 2a - Cars were driven through the State 11-mode cycle on the Los Angeles River Bottom (dry season). Samples were collected by proportional sampler.
- 2b - Cars were driven through the State 11-mode cycle on the Los Angeles River Bottom. Composite NO_x samples were collected manually during cruise and acceleration modes.
- 3b - Cars were driven through 8-mode cycle on dynamometer. Composite NO_x samples were collected manually during cruise and power modes.

The means, standard deviations, and upper and lower 95% confidence limits of the NO_x emissions determined by the different procedures are shown in Table I.

Table I
OXIDES OF NITROGEN CONCENTRATIONS
BY DESIGNATED PROCEDURES

	1a	2a	2b	3b
ALL CARS				
Mean	1,364	1,199	1,414	1,463
Standard Deviation	460	460	528	533
95% Confidence Limits				
On mean				
lower	1,185	1,021	1,205	1,239
upper	1,542	1,378	1,623	1,686
On individual				
lower	421	256	327	323
upper	2,302	2,143	2,501	2,603
STANDARD CARS				
Mean	1,499	1,265	1,541	1,543
Standard Deviation	502	533	574	672
95% Confidence Limits				
On mean				
lower	1,241	991	1,235	1,172
upper	1,757	1,539	1,847	1,914
On individual				
lower	425	136	318	105
upper	2,563	2,395	2,764	2,981
COMPACT CARS				
Mean	1,154	1,098	1,229	1,354
Standard Deviation	297	316	408	332
95% Confidence Limits				
On mean				
lower	955	886	955	1,130
upper	1,354	1,310	1,503	1,577
On individual				
lower	492	394	320	613
upper	1,816	1,801	2,138	2,094

Source: Report to the Steering Committee, Los Angeles Test Station Project by Charles S. Tuesday, June 10, 1963.

The correlation between pairs of sampling procedures are shown below in Table II.

Table II
COMPARISON OF RESULTS WITH DIFFERENT PROCEDURES

	3b/1a	3b/2a	3b/2b	1a/2a	1a/2b	2a/2b
ALL CARS						
Ratio of the Means	1.07	1.22	1.03	1.14	0.97	0.85
Correlation Coefficients	0.844	0.918	0.921	0.887	0.886	0.871
STANDARD CARS						
Ratio of the Means	1.03	1.22	1.00	1.19	0.97	0.82
Correlation Coefficients	0.863	0.939	0.955	0.891	0.906	0.930
COMPACT CARS						
Ratio of the Means	1.17	1.23	1.10	1.05	0.94	0.89
Correlation Coefficients	0.808	0.830	0.884	0.935	0.772	0.716

Source: In part, from Report to the Steering Committee Los Angeles Test Station Project, by Charles S. Tuesday, June 10, 1963.

The NO_x concentration from 11 vehicles was measured for each of the power modes of the 8-mode cycle. The results are tabulated in Table III. As shown, the emissions are highest during acceleration, and are directly related to vehicle speed. This is in agreement with results obtained from other emissions surveys and from studies using test engines.

Table III
OXIDES OF NITROGEN CONCENTRATIONS BY MODE OF OPERATION
(ppm NO₂)

CAR NUMBER	TYPE OF TRANSMISSION	15-30 mph ACCELERATION	0-25 mph ACCELERATION	15 mph CRUISE	30 mph CRUISE	50 mph CRUISE
27	MANUAL	1,512	1,526	70	616	1,405
28	MANUAL	2,179	1,576	95	1,108	2,379
1005	MANUAL	1,068	646	45	296	339
1021	MANUAL	2,198	1,279	88	807	2,190
29	AUTOMATIC	2,724	2,200	1,378	1,834	2,712
1001	AUTOMATIC	617	801	53	332	664
1002	AUTOMATIC	1,217	448	37	747	2,132
1003	AUTOMATIC	1,353	314	48	248	1,071
1004	AUTOMATIC	2,276	2,040	199	815	1,157
1006	AUTOMATIC	2,368	1,730	174	1,831	2,050
1018	AUTOMATIC	1,129	1,157	260	1,146	1,279
Average		1,694	1,247	204	889	1,581

Table IV shows the mean emission of exhaust NO_x measured on 8-mode cycle during the mass testing phase. Oxides of nitrogen composite samples were collected by means of a specially designed sampler, and were analyzed by the phenoldisulfonic acid (PLS) method.

The means shown are simple averages and have not been adjusted for types of transmission, the population profile, the percent CO + CO₂ or other factors which can affect the average emissions of oxides of nitrogen.

Table IV
AVERAGE EXHAUST EMISSIONS OF
OXIDES OF NITROGEN
BY TEST GROUPS OF VEHICLES

TEST GROUP	NUMBER OF VEHICLES	ppm NO ₂
General Public ¹	709	997
Auto Club Employees	67	1,158
Pickup Trucks	22	964
Auto Club Owned	5	1,798

¹Vehicles brought in by auto club members for speedometer check.

The cumulative frequency distribution of emissions by transmission type, weighted according to the number of cars in each category, are shown in Table V.

Table V
FREQUENCY DISTRIBUTION OF EMISSIONS OF OXIDES OF NITROGEN
BY TYPE OF TRANSMISSION
(ppm NO₂)

TYPE OF TRANSMISSION	NUMBER OF VEHICLES	PERCENT OF VEHICLES EMITTING HIGHER CONCENTRATION THAN VALUE SHOWN											Mini- max	Mean
		Mini- max	90	80	70	60	50	40	30	20	10	Mini- max		
Manual	228	65	275	465	585	705	845	960	1,155	1,405	1,780	2,430	870	
Automatic	553	20	360	555	725	890	1,010	1,175	1,330	1,580	1,860	3,210	1,075	
All Vehicles	781	20	325	510	670	820	950	1,110	1,250	1,530	1,790	3,210	1,015	

Source: Adapted from a report to the Steering Committee, Los Angeles Test Station Project by Charles E. Zimmer, October 8, 1963.

Table VI summarizes the NO_x emissions from cars classed according to weight-to-engine displacement ratio (gross weight of automobile, in pounds, divided by the engine displacement in cubic inches). Of the vehicles equipped with manual transmissions, those having a weight-to-displacement ratio between 12.0 - 15.9 emitted the highest concentrations of NO_x.

Table VI
WEIGHTED AVERAGE NITROGEN OXIDE EMISSIONS BY RATIO OF GROSS WEIGHT
TO ENGINE DISPLACEMENT

(ppm NO₂)

RATIO: GROSS WEIGHT TO ENGINE DISPLACEMENT	AUTOMATIC TRANSMISSION			MANUAL TRANSMISSION		
	Number of Vehicles	Mean	Standard Deviation	Number of Vehicles	Mean	Standard Deviation
8.0- 9.9	17	1,072	452	3	393	124
10.0-11.9	239	1,067	606	29	610	314
12.0-13.9	210	1,093	560	97	939	486
14.0-15.9	59	1,039	536	71	911	529
16.0-17.9	18	1,014	493	15	667	326
Unknown	10					
All Vehicles		1,075	575		870	450

Source: See Table V.

Analyses of the Test Station Project results disclosed a statistically significant difference in the mean levels of NO_x for cars of different types of transmission. As shown in Table VI, the mean NO_x concentration was 1075 ppm for cars with automatic transmission compared with 870 ppm for cars with manual transmission.

Based on statistics reported in Automotive News Almanac⁽¹⁾ in 1962, 63% of the U.S. made cars were equipped with automatic transmission. The weighted average for the 1962 car population is therefore:

$$(1075)(0.63) + (870)(.37) = 1000 \text{ ppm}$$

COORDINATING RESEARCH COUNCIL SURVEY

In 1956, the Coordinating Research Council, Inc. (CRC) tested 272 vehicles. Exhaust gases were sampled for NO_x during four power modes, and the NO_x content analyzed by the PDS method.

The summary of the oxides of nitrogen emissions shown in Table VII was reproduced from the CRC report.⁽²⁾

Table VII

SUMMARY OF OXIDES OF NITROGEN EMISSIONS BY MODE OF OPERATION

(ppm NO₂)

CONDITION	50 mph CRUISE	30 mph CRUISE	15-30 mph ACCELERATION	20-45 mph ACCELERATION
Number of Samples	266	271	274	269
Average Emissions Pounds Per Hour	0.577	0.178	0.506	0.703
Average Emissions PPM	1,625	905	1,700	1,185
Includes 2.5% of Samples	90	104	110	166
Includes 97.5% of Samples	3,774	2,338	3,564	2,742

CALIFORNIA DEPARTMENT OF PUBLIC HEALTH SPECIALIZED VEHICLE STUDY

In 1963, the California Department of Public Health contracted with the Los Angeles County Air Pollution Control District to investigate emissions from three groups of specialized vehicles - a group of 15 U.S. compact cars, a group of 50 foreign compact cars and a group of 10 U.S. light trucks. Of the U.S. compacts, 5 had automatic and 10 had manual transmission. Foreign compacts and American trucks were equipped with manual transmission.

Measurements of oxides of nitrogen in exhaust were made during two power modes - 40 mph cruise, and 15-30 mph acceleration. The samples were analyzed by the PDS method.

The results from the Specialized Vehicle Survey are summarized in Tables VIII, IX, and X. As shown, the average oxides of nitrogen concentration in the exhaust of 15 U.S. compacts, operated at 15-30 mph, is very close to the CMC results for this mode. The foreign compacts and U.S. trucks had lower emissions. These latter vehicles were all equipped with manual transmission.

Table VIII
NITROGEN OXIDE CONCENTRATION BY TYPE OF TRANSMISSION
AND MODE OF OPERATION
UNITED STATES COMPACT CARS
(ppm NO₂)

	AUTOMATIC TRANSMISSION		MANUAL TRANSMISSION		ALL CARS	
	15-30 mph Acceleration	40 mph Cruise	15-30 mph Acceleration	40 mph Cruise	15-30 mph Acceleration	40 mph Cruise
Number of Cars	5	5	10	10	15	15
Mean	2,133	1,608	1,452	1,375	1,679	1,453
Median	2,200	1,540	1,395	1,405	1,561	1,533
Standard Deviation	1,063	708	525	500	781	563
Smallest Value	769	637	558	719	558	637
Largest Value	3,639	2,629	2,383	2,457	3,639	2,629
Range	2,870	1,992	1,825	1,738	3,081	1,992

Table IX
NITROGEN OXIDE CONCENTRATION
BY MODE OF OPERATION
FOREIGN COMPACT CARS
MANUAL TRANSMISSION ONLY
(ppm NO₂)

	15-30 mph Acceleration	40 mph Cruise
Number of Cars	50	50
Mean	1,213	753
Median	1,136	634
Standard Deviation	581	543
Smallest Value	102	71
Largest Value	2,829	2,880
Range	2,727	2,809

Table X
NITROGEN OXIDE CONCENTRATIONS IN EXHAUST
BY MODE OF OPERATION
UNITED STATES LIGHT TRUCKS
MANUAL TRANSMISSION

(ppm NO₂)

	15-30 mph Acceleration	40 mph Cruise
Number of Trucks	10	10
Mean	1,456	1,019
Median	1,391	1,091
Standard Deviation	492	460
Smallest Value	783	294
Largest Value	2,577	1,844
Range	1,794	1,550

EMISSIONS OF NO_x FROM DIESELS

Emissions of oxides of nitrogen from diesels have not been comprehensively studied. The few limited studies that have been made are mostly on laboratory test engines. An exception to these is the study of exhaust emissions from diesel, gasoline and propane powered coaches during city driving.⁽³⁾ A review by the Department in 1962 of all data available revealed that NO_x concentrations in diesel exhaust were lower than those in gasoline exhaust under comparable operating conditions; however, because diesels emit larger volumes of exhaust, the mass emission of NO_x from diesels may be slightly higher.⁽⁴⁾

A recent study of emissions from laboratory engines and truck-mounted engines under a variety of operating conditions shows the maximum NO concentration detected to be 1100 ppm. This is about half the maximum NO concentration measured in gasoline exhaust.⁽⁵⁾ In this study, as well as others, it was found that most of the oxides of nitrogen emitted were in the form of nitric oxide.

NO_x emissions from diesel vehicles have been shown to vary considerably depending on engine type, engine design and loading, and other factors. The limited data available are not adequate for delineating the exact role of diesel emissions in air pollution and for establishing emission standards. They do indicate that the mass emission of NO_x from diesels is about the same or slightly higher than emissions from gasoline vehicles.

ESTIMATES OF MASS EMISSIONS OF NO_x FROM MOTOR VEHICLES

The total weight of oxides of nitrogen emitted daily from motor vehicles in a community may be estimated by multiplying the total motor fuel consumption in gallons per day by an average NO_x emission factor in pounds per gallon of fuel. The emission factor for Los Angeles vehicles is derived as follows:

Studies of D'Alleva,⁽⁶⁾ and the more recent one by Leonard,⁽⁷⁾ indicate that A/F ratios are relatable to CO and CO₂ concentrations in exhaust. According to the method suggested by Leonard, and assuming that the method is applicable to weighted average concentrations obtained from a combination of operating modes, the wet basis CO and CO₂ concentrations of 3.42 and 11.3 respectively (Test Station averages) would correspond to an A/F ratio of 13 to 1. This is confirmed by actual road test data which indicate that the A/F ratio for a random sample of Los Angeles vehicles is 12.9:1.⁽⁸⁾ With vehicles operated at this A/F ratio on the road, the average NO_x concentration in exhaust is 975 ppm.⁽⁹⁾

The specific gravity of gasoline referred to as Los Angeles "basin mix" has been reported to be 0.745, corresponding to a density of 6.2 pounds per gallon.⁽¹⁰⁾ On this basis, the average volume of intake air per gallon of fuel consumed would equal:

$$13.0 \text{ lb/lb} \times 6.2 \text{ lb/gal} \times \frac{1}{29} \times 379 \text{ cf/mol} = 1053 \text{ cf of air/gal}$$

Assuming that the average exhaust volume equals the average intake air volume, the weight of NO_x emitted (determined as NO₂) therefore equals:

$$1053 \frac{\text{cf}}{\text{gal}} \times \frac{1000}{106} \times \frac{46 \text{ lb/mol}}{379 \text{ cf/mol}} = 0.13 \text{ lb/gal}$$

For the 1963 Los Angeles vehicle population, the gross oxides of nitrogen emissions would then equal:

$$0.13 \frac{\text{lb}}{\text{gal}} \times 7 \times 10^6 \text{ gal/day} \times \frac{1}{2000 \text{ lb/ton}} = 455 \text{ tons/day}$$

Similarly calculated, the emissions of NO_x from motor vehicles in the San Francisco Bay Area equal 236 tons per day, in San Diego County 66 tons per day, in Sacramento 40 tons per day, and in Riverside 23 tons per day.

The estimates of motor vehicle fuel consumed include both gasoline and diesel fuel. It is assumed in the calculation that the combustion of a gallon of diesel fuel produces the same quantity of oxides of nitrogen as the combustion of a gallon of gasoline. Approximately 5% of the motor vehicle fuel sold in California is for use in diesels.

The average emission factor of 0.13 lbs of NO_x emitted, per gallon of fuel consumed, was based on results obtained from the L.A. Test Station

Project which is the most recent and most comprehensive study. It should be noted that the average concentrations of NO_x , CO, and CO_2 were obtained for the present Los Angeles car population tested on operating conditions purported to represent Los Angeles driving patterns. It is assumed that the vehicle distribution and the driving patterns, and, hence, the emission factor derived for conditions in Los Angeles is applicable to other areas of the state in calculating the total oxides of nitrogen emissions.

Not taken into consideration in estimating mass emissions of NO_x is the possible effect of cold starts on NO_x emissions. For example, a car left standing for a long period, such as overnight, may emit lower concentrations of NO_x during the first few minutes. What effect cold starts may have on the total emissions, therefore, is not known.

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Chapter III

OXIDES OF NITROGEN FROM STATIONARY SOURCES

The wide spectrum of stationary combustion processes which discharge oxides of nitrogen ranges from small domestic gas appliances to large thermal power plants. In between these extremes is a large variety of industrial and commercial processes. Stationary sources have been categorized by the Los Angeles County Air Pollution Control District according to mass emissions of NO_x per hour as follows:

Small sources - those emitting NO_x at a rate of less than 5 pounds per hour.

Medium sources - those emitting NO_x at a rate between 5 to 100 pounds per hour.

Large sources - those emitting NO_x at a rate greater than 100 pounds per hour.

In the "small sources" category are included the domestic and commercial gas appliances. The number of these appliances and, hence, the emissions from this group are directly relatable to population growth. On the average, discharge volume from these appliances is small and the oxides of nitrogen concentration in the flue gases is about 50 ppm; hence, individually, these appliances emit a very small quantity of oxides of nitrogen. But there is such a large number of these appliances in every community that, collectively, they represent a significant source of NO_x .

Also included in the "small sources" category are some metallurgical furnaces, non-metallurgical kilns, stationary internal combustion engines handling light loads, and some chemical processes. How much of the total NO_x emissions is attributable to these sources depends on the number of industries which employ equipment in the "small sources" category. In most communities, there is at least some light industry where this kind of equipment is employed.

In the "medium sources" category are larger industrial furnaces (open-hearth steel furnaces and glass furnaces), asphalt paving plants, large incinerators, refinery heaters, and stationary internal combustion engines in the 300 to 1799 H.P. class used for driving compressors.

The average concentration of NO_x in the flue gases from this category of equipment ranges from 50 to 2000 ppm. As this equipment is used in a wide variety of industrial activities, NO_x emissions attributable to this class differ greatly from community to community, depending on the extent and nature of industrial development. In rural regions, the quantity and proportion of NO_x emissions from this class tend to be small.

Of the oxides of nitrogen emanating from stationary sources, those discharged from equipment in the "large sources" category account for the largest proportion of the total. Large manufacturing industries and thermal power plants are in this category. Emissions from power plants generally vary with the seasons - greater in winter, less in summer.

In communities where industrialization is not highly developed, and where large thermal power plants are absent, emissions from stationary sources would be a comparatively small fraction of the total.

As shown, NO_x emissions are higher in winter than in summer. In Los Angeles, the increase of NO_x emissions in the winter over the summer amounts to 60%. This is the result of increased emissions from thermal power generation to satisfy a higher electrical demand during winter months.

Table I shows the data provided by air pollution control districts on oxides of nitrogen emissions from several California regions during summer and winter months.

Table I
EMISSIONS OF OXIDES OF NITROGEN FROM STATIONARY SOURCES
FOR SELECTED CALIFORNIA REGIONS - 1964
(Tons per day)

SOURCE	LOS ANGELES		BAY AREA	SAN DIEGO		SACRAMENTO		RIVERSIDE	
	Summer	Winter	Annual Average	Summer	Winter	Summer	Winter	Summer	Winter
TOTAL	226	375	214	31	39	4	10	7	9
LARGE SOURCES									
Power Plants	94	162	84	17	23				
Others	6	6	4						
Subtotal	100	168	88	17	23				
MEDIUM SOURCES									
Industrial Stationary (Internal Combustion Engines)	31	49	28						
Subtotal	27	27	16						
	58	76	44						
SMALL SOURCES									
Domestic and Commercial	11	27	22	5	7	2	8		
Industrial	48	95	47	4	4	1	1		
Miscellaneous			1			1	1		
Subtotal	59	122	70	9	11	4	10		
Miscellaneous Sources	9	9	12	5	5			3	3

Chapter IV

INCREASES IN OXIDES OF NITROGEN EMISSIONS

As with community air pollution in general, future increases in oxides of nitrogen emissions are inextricably linked with the growth of population and increases in motor vehicle registrations and fuel consumption. Projections of future increases in the oxides of nitrogen must therefore take into account the trends in these related factors.

The population of California has approximately doubled every twenty years since 1860. Shortly after 1940, because of this growth and its attendant increase of fuel consumption, air pollution became increasingly noticeable in large metropolitan areas in California.

POPULATION GROWTH

The population of the State has more than doubled from 1940 to the present. Today, the less densely populated counties are growing at an even more rapid rate than the more densely populated areas such as Los Angeles County, the San Francisco Bay Area or even the State of California as a whole. By 1980 the populations of Riverside, Sacramento, and San Diego Counties are expected to be six times their population in 1940 while the population of the State and of Los Angeles and the Bay Area, in 1980, is expected to be only three to four times their 1940 population.

MOTOR VEHICLE INCREASE

Meanwhile, the increase in motor vehicle registration is outstripping even that of the population. Motor vehicles increased from 2.8 million in 1940 to the present 9.6 million. By 1980 it is expected that approximately 16 million vehicles will be registered in California - five times the 1940 figure. In some counties, the growth is even more rapid. An eight-fold increase is expected in the smaller counties by 1980. Riverside County, for example, is expected to have, in 1980, eight times more motor vehicles than in 1940.

The data on population and motor vehicle registration for each year since 1940 are shown in Tables I and II for the State, Los Angeles County, San Diego County, Riverside County, Sacramento County, and the San Francisco Bay Area. (The Bay Area Air Pollution Control District at present includes the counties of Alameda, Contra Costa, Marin, San Francisco, San Mateo, and Santa Clara.)

Table I
ESTIMATED POPULATION
CALIFORNIA 1940-1964 WITH PROJECTIONS FOR 1970, 1975 AND 1980
AS OF DECEMBER 31 EACH YEAR

(In thousands)

YEAR	STATE	LOS ANGELES COUNTY	BAY AREA (6 COUNTIES)	SAN DIEGO COUNTY	SACRAMENTO COUNTY	RIVERSIDE COUNTY		
1940	7,094	2,872	1,637	298	176	109		
1941	7,486	2,975	1,699			111		
1942	8,121	3,322	2,042			125		
1943	8,726							
1944	9,145							
1945	9,452	3,517	2,359			143		
1946	9,696	3,921	2,295			155		
1947	9,948							
1948	10,201							
1949	10,491	4,071	2,350					
1950	10,887	4,235	2,510	576	287	176		
1951	11,384	4,401	2,564	714	310	184		
1952	11,870	4,626	2,637	756	330	198		
1953	12,309	4,862	2,701	763	346	211		
1954	12,761	5,080	2,760	787	364	224		
1955	13,288	5,285	2,838	836	386	238		
1956	13,879	5,501	2,938	873	408	254		
1957	14,459	5,697	3,042	915	432	271		
1958	15,015	5,854	3,149	970	460	288		
1959	15,576	5,996	3,257	1,023	493	304		
1960	16,158	6,149	3,354	1,070	524	321		
1961	16,774	6,317	3,499	1,113	553	340		
1962	17,360	6,493	3,625	1,140	576	360		
1963	17,974	6,692	3,759	1,158	594	379		
1964	18,563	6,836		1,209	624			
1970	22,034	7,731	4,610	1,428	783	516		
1975	25,034	8,531	5,301	1,613	926	620		
1980	28,437	9,342	5,990	1,820	1,083	732		

Note: The estimates in the table above were adjusted to December 31 of each year by the Bureau of Air Sanitation from the sources shown below.

Source: 1940, 1950 and 1960, decennial reports of the U.S. Bureau of the Census, as of April 1, each year.
1941 through 1948 for Los Angeles, Riverside and the Bay Area Counties are from the California Taxpayers Association as of January 1 of the following year.
The 1951-1959 intercensal, the 1961-1964 postcensal estimates and the estimates for 1970, 1975 and 1980 all as of July 1, each year, were prepared by the Financial and Population Research Section, Department of Finance.

Table II
MOTOR VEHICLE REGISTRATIONS
CALIFORNIA AND SELECTED AREAS
1940-1964, WITH PROJECTIONS FOR 1970, 1975 AND 1980
AS OF DECEMBER 31, EACH YEAR

(In thousands)

YEAR	STATE	LOS ANGELES COUNTY	BAY AREA (6 COUNTIES)	SAN DIEGO COUNTY	SACRAMENTO COUNTY	RIVERSIDE COUNTY
1940	2,803	1,173	572	114	68	42
1941	2,993	1,262	605	135	71	45
1942	2,869	1,214	565	141	69	41
1943	2,786	1,167	591	137	68	42
1944	2,818	1,170	595	137	70	44
1945	2,893	1,192	605	140	71	46
1946	3,140	1,302	636	148	79	52
1947	3,525	1,463	710	164	90	59
1948	3,805	1,572	775	179	99	64
1949	4,159	1,696	851	198	110	69
1950	4,618	1,882	945	221	125	75
1951	4,919	2,006	1,007	242	137	79
1952	5,147	2,096	1,040	265	147	85
1953	5,497	2,269	1,097	285	159	93
1954	5,692	2,382	1,126	294	165	98
1955	6,181	2,600	1,218	316	182	110
1956	6,526	2,716	1,281	341	194	118
1957	6,826	2,826	1,335	369	206	125
1958	7,293	2,937	1,432	405	227	137
1959	7,393	2,967	1,453	428	240	143
1960	7,833	3,110	1,543	455	256	151
1961	8,117	3,184	1,599	474	271	158
1962	8,768	3,373	1,736	508	307	176
1963	9,050	3,489	1,813	511	308	182
1964	9,565	3,642	1,887	543	324	204
1970	11,700	4,400	2,300	700	430	270
1975	13,600	5,000	2,700	820	500	320
1980	15,500	5,600	3,000	920	570	360

Source: State of California, Department of Motor Vehicles Report, "Number of Vehicles Registered," December 31, 1940 through December 31, 1964. Projections for 1970, 1975 and 1980 are by Bureau of Air Sanitation, based on Trend of Registrations 1955-1964.

FUEL CONSUMPTION

Estimates of future fuel consumption, using various approaches, have been reported in the literature. These range from the conservative linear projections based on the trend of the past few years⁽¹⁾ to those based on the logarithmic method.⁽²⁾⁽³⁾ The estimates to be reported here are the result of compromises between the estimates obtained by the two extremes and are very close to the results obtained by the exponential method.⁽⁴⁾

Fuel consumption statistics are available only on a statewide basis. Thus, it is necessary to use the percentage of county-to-state motor vehicle registration as the method of apportioning the State total fuel consumption to a county. Figure 1 illustrates the percent increase since 1940 of the motor vehicle fuel consumption in the State and in five areas in the State.

While the State population is growing rapidly, as shown in Figure 2, it is not as fast as the growth of motor vehicle registration. The rate of fuel consumption is even more rapid.

The data on motor vehicle fuel consumption for the State as a whole are shown in Table III. In 1964, more than 19 million gallons of fuel were consumed daily in the State. The 1970, 1975, and 1980 fuel consumption rates are projections based on the 1955-1964 trend.

Table IV shows the quantity of electrical power produced in the State and how much is being utilized per capita. In 1940, 1380 KW-Hr/Yr of power per capita was produced. By 1961 this use tripled to 4140, and it is expected to reach more than five-fold by 1980. Compared to 1940, per capita power production is expected to increase 33 percent faster than population by 1980.

GROWTH TREND OF NO_x

Table V shows amounts of motor vehicle emissions, of current date, and amounts projected to the years 1970 and 1980. The projections are based on the State of California figures for fuel consumption trends and for apportionment of county-to-state population. The figures presented are for warm starts and do not take into account possible modifications of engine and exhaust systems, the increased use of automatic transmission, or possible changes in traffic patterns - any or all of which may affect the amounts of NO_x emitted.

Table V also presents projections of emissions from stationary sources based on trends in population growth. The figures do not take into account possible changes in the current means for meeting population demand for power.

Figure 1
MOTOR VEHICLE FUEL CONSUMPTION TREND
CALIFORNIA AND SELECTED AREAS
1940-1964

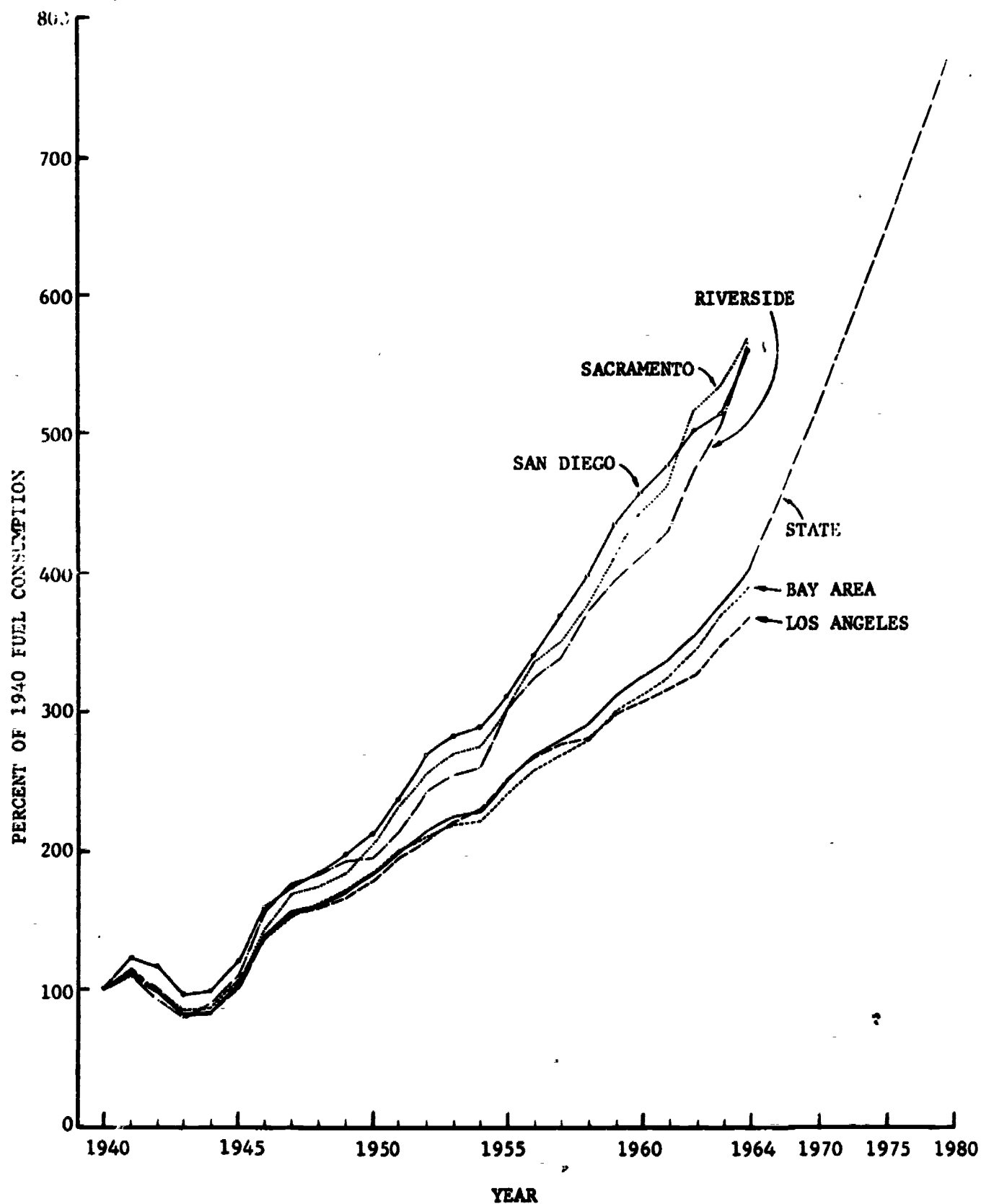


Figure 2
RATES OF GROWTH
CALIFORNIA, 1940 - 1964

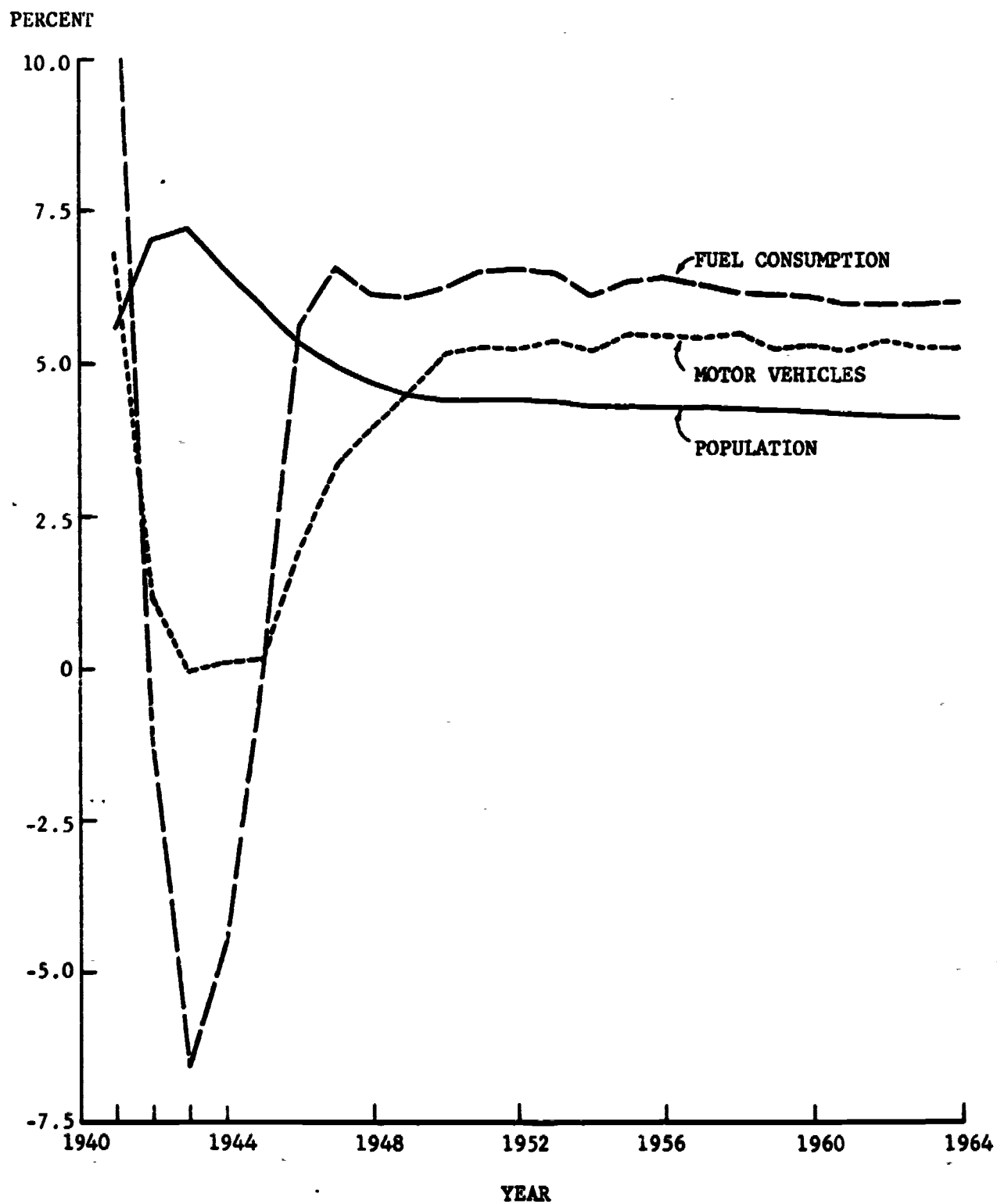


Table III

MOTOR VEHICLE FUEL CONSUMPTION
CALIFORNIA, 1940-1964
WITH PROJECTIONS FOR
1970, 1975 AND 1980

YEAR	THOUSANDS OF GALLONS PER YEAR	YEAR	THOUSANDS OF GALLONS PER YEAR
1940	1,758,330	1955	4,405,613
1941	1,978,547	1956	4,741,045
1942	1,719,162	1957	4,934,102
1943	1,434,560	1958	5,136,756
1944	1,467,906	1959	5,456,202
1945	1,810,425	1960	5,691,028
1946	2,436,431	1961	5,935,774
1947	2,735,932	1962	6,252,766
1948	2,830,124	1963	6,634,403
1949	2,990,504	1964	7,076,252
1950	3,212,615	1970	9,000,000
1951	3,505,873	1975	11,200,000
1952	3,754,560	1980	13,500,000
1953	3,948,445		
1954	4,032,352		

1. Motor vehicle fuel consumption figures for 1940-1963 are taken from 1964 California Statistical Abstract. The figure for 1964 is reported by State Board of Equalization.
2. Figures represent statewide sale for on-highway use for motor vehicles including gasoline, L.P.G., and diesel fuel, less estimated gallonage upon which refunds of tax were made because of nonhighway use.
3. Estimates of 1970, 1975, and 1980 fuel figures are Bureau of Air Sanitation projections.

Table IV
ANNUAL PRODUCTION OF ELECTRICAL ENERGY
CALIFORNIA, 1940-1962

YEAR	TOTAL MILLIONS OF KILOWATT HOURS	KILOWATT HOURS PER CAPITA	PERCENT OF 1940 KILOWATT HOURS PER CAPITA
1940	9,789	1380	100
1941	10,438	1394	101
1942	11,583	1426	103
1943	14,776	1693	123
1944	15,887	1737	126
1945	15,944	1687	122
1946	17,314	1786	129
1947	19,432	1953	142
1948	20,287	1989	144
1949	22,112	2108	153
1950	24,836	2281	165
1951	29,375	2580	187
1952	29,252	2464	179
1953	35,064	2849	206
1954	37,762	2959	214
1955	42,512	3199	232
1956	46,679	3363	244
1957	49,901	3451	250
1958	50,782	3382	245
1959	58,113	3731	270
1960	63,834	3951	286
1961	69,444	4140	300
1962	73,554	4237	307

Source: California Statistical Abstract,
1964.

Table V
ESTIMATED EMISSIONS OF OXIDES OF NITROGEN
FOR SELECTED CALIFORNIA REGIONS IN 1964, WITH PROJECTIONS TO 1970 AND 1980
(Tons per day)

	LOS ANGELES		SAN FRANCISCO BAY AREA	SAN DIEGO		SACRAMENTO		RIVERSIDE	
	Summer	Winter		Summer	Winter	Summer	Winter	Summer	Winter
1964									
Total	706	855	463	103	111	47	53	34	36
Stationary Sources	226	375	214	31	39	4	10	7	9
Motor Vehicles	480	480	249	72	72	43	43	27	27
Percent of Total									
Due to Motor Vehicles	68	56	54	70	65	91	81	79	75
1970 (estimated) ¹									
Total	860	1,020	570	140	150	<70	70	<50	50
Stationary Sources	260	420	250	40	50	<10	10	<10	10
Motor Vehicles	600	600	320	100	100	60	60	40	40
Percent of Total									
Due to Motor Vehicles	70	59	56	71	67	>86	86	>80	80
1980 (estimated) ¹									
Total	1,180	1,380	800	190	200	<100	110	70	80
Stationary Sources	310	510	330	50	60	<10	20	10	20
Motor Vehicles	870	870	470	140	140	90	90	60	60
Percent of Total									
Due to Motor Vehicles	74	63	59	74	70	>90	82	86	75

¹ To the nearest 10 tons.

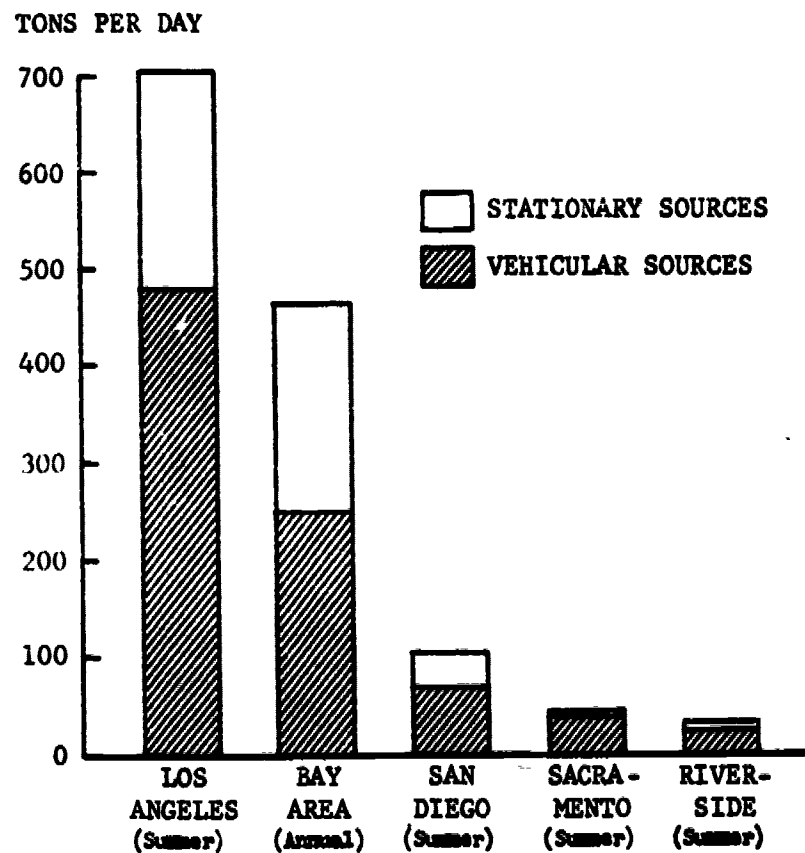
Although the amount of vehicle use and industrial activity is not significantly affected by seasonal changes, the need for power generation and space heating is so influenced. During the winter months increased amounts of fuel are required and this influences the amounts of NO_x emitted to the atmosphere. The figures in Table V reflect this.

In areas where electrical energy is not generated by thermal power plants, there are fewer seasonal variations in NO_x emissions. In these communities the oxides of nitrogen due to motor vehicles is a high proportion of the total. For example, approximately 90% of the NO_x emissions in Sacramento are from motor vehicles contrasted to 60% in Los Angeles. Figure 3 illustrates the contribution of vehicular and stationary source emissions in five California areas.

Figure 3

ESTIMATED EMISSIONS OF OXIDES OF NITROGEN
1964

(Tons per day)



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Chapter V

OXIDES OF NITROGEN IN THE ATMOSPHERE

Air monitoring for nitrogen dioxide in California began in 1951 when the Los Angeles County Air Pollution Control District initiated a hand sampling program. With the development of continuous measuring and recording instruments, it became possible in 1956 to monitor nitric oxide (NO) and nitrogen dioxide (NO₂) at different locations, both simultaneously and continuously. Since then, measurement of these two compounds with continuous air monitoring instruments has been made at one time or another at 37 locations in the state.

Currently there are 24 stations in operation, 21 measuring both oxides of nitrogen (NO_x) and nitrogen dioxide (NO₂), and three others measuring NO or NO₂ individually. Sixteen of the 24 stations comprise the State-wide Cooperative Air Monitoring Network (SCAN) which samples other pollutants besides oxides of nitrogen. The network is coordinated by the California Department of Public Health which operates some of the stations and provides varying degrees of support and assistance to air pollution control districts which operate the other stations. The locations of the air monitoring stations are shown in Figure 1.

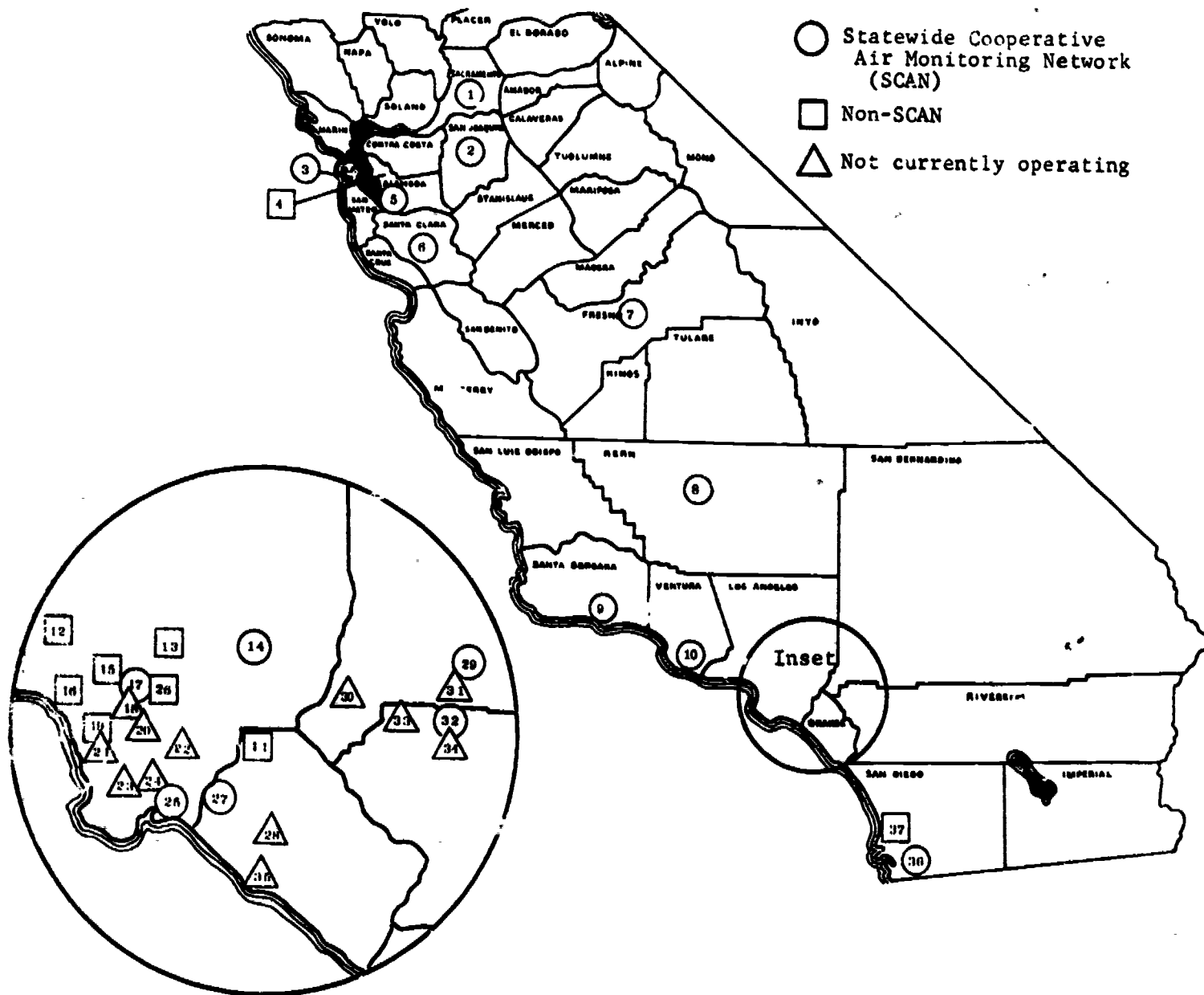
The air monitoring instruments used to measure oxides of nitrogen are basically the same throughout California. Nitrogen dioxide in a metered air stream is absorbed in a metered stream of reagent to produce a red dye.⁽¹⁾ The intensity of the color is continuously measured with a photometer and recorded on a strip chart.⁽²⁾

As the photometer has a logarithmic response to concentration, the method has a high sensitivity to low concentrations combined with a relatively high range. Most monitoring instruments now in use have a range of 0-3 or 0-4 ppm oxides of nitrogen. At the low end of the scale, the difference of concentration that can be detected is in the order of 0.01 ppm; at the high end, it is 0.2 ppm.

Oxides of nitrogen (NO_x) concentrations are usually determined with the same instrument that measures nitrogen dioxide. To analyze the NO_x (NO + NO₂) concentration in an air sample, it is first passed through a converter where nitric oxide is oxidized to nitrogen dioxide which is then analyzed with the system just described. Thus, by using a parallel system of two columns, one for NO₂, one for the sum of NO + NO₂, it is possible to determine nitric oxide concentration differentially.

The instruments used by the various air monitoring agencies are basically the same, although air reagent columns, NO converters, and electrical hookups for differential quantitation of NO, NO_x, and NO₂ do

Figure 1
LOCATION OF AIR MONITORING STATIONS IN CALIFORNIA



STATION IDENTIFICATION

1	Sacramento	14	Azusa	26	U.S.C. Medical Center
2	Stockton	15	Hollywood Freeway	27	Anaheim
3	San Francisco	16	West Los Angeles	28	Santa Ana Airport
4	Berkeley	17	Downtown Los Angeles	29	San Bernardino
5	Oakland	18	Vernon	30	Ontario
6	San Jose	19	Inglewood	31	Rialto
7	Fresno	20	Florence	32	Riverside
8	Bakersfield	21	Lennox	33	Mira Loma
9	Santa Barbara	22	Downey	34	U.C. at Riverside
10	Ventura	23	Torrance	35	Newport Beach
11	La Habra	24	Avalon Village	36	San Diego
12	Burbank	25	N. Long Beach	37	Mission Beach
13	Lasadena				

vary. Instrument operation, however, has not been standardized; hence, data obtained by different agencies differ in quantity and reliability. Those agencies devoting the most efforts to the task usually produce the most reliable and continuous data. With the State coordinating the operation of many of the stations in recent years, some degree of standardization has been achieved. As a result, the recent data collected in the statewide air monitoring network are more suitable for comparing pollution in the various communities and, hence, they are used in this report.

Maximum hourly averages of NO_x of 0.25 ppm or higher occur often in large California cities. During the 1963-64 period, they occurred more than 100 days per year in Los Angeles, Long Beach, Oakland, and San Jose. The combined NO and NO_2 was not measured in San Francisco. Maximum hourly averages of 1.00 ppm or higher, however, occur 5 days or less per year in these same cities. Table I shows the number of days per year having maximum concentrations greater than specified concentrations of NO_x and NO_2 . Maximum hourly averages of NO_2 , of 0.25 ppm or higher, occurred at a rate of 20 or more days per year in three cities - Los Angeles, Long Beach, and San Francisco.

Table I

OXIDES OF NITROGEN
AVERAGE NUMBER OF DAYS PER YEAR HAVING MAXIMUM HOURLY
AVERAGE CONCENTRATIONS GREATER THAN
SPECIFIED CONCENTRATIONS
SCAN, 1963-64

Location	OXIDES OF NITROGEN (NO_x), PPM				NITROGEN DIOXIDE (NO_2), PPM		
	0-.24	>.25	>.50	>1.00	0-.24	>.25	>.50
Los Angeles	164	201	89	5	336	29	3
Long Beach	191	174	92	5	339	26	3
Oakland	252	113	32	3	359	6	-
San Diego	289	76	18	1	362	3	-
Riverside	296	69	14	3	356	9	-
Sacramento	298	67	19	1	362	3	-
Stockton	319	46	11	1	365	-	-
San Jose	237	128	26	-	355	10	-
San Francisco	-	-	-	-	345	20	-
Fresno	312	53	7	-	360	5	-
Azusa	341	35	3	-	361	4	-
Bakersfield	324	41	-	-	365	-	-
Anaheim	349	16	-	-	365	-	-
Santa Barbara	355	12	-	-	365	-	-
Ventura	361	4	-	-	365	-	-
San Bernardino	364	1	-	-	365	-	-

The total number of hours during 1963 and 1964 having maximum hourly average concentrations in specified ranges are shown in Table II as are the percentage of the readings. In Long Beach, for example, of approximately 14,000 hourly readings in 1963-1964, 3,179 maximum hourly readings were higher than 0.25 ppm which is equivalent to 22% of the total hours.

Although they may be of short duration, the record high peak concentrations are indicative of the contamination levels that may be reached at an air monitoring station under present emission levels and at the most adverse conditions of weather. With more persistent stable weather conditions, the duration of the peak concentration would increase and so might the peak concentration itself. The maximum oxides of nitrogen and nitrogen dioxide that have been observed since continuous air monitoring for these gases began are shown in Figure 2 and Figure 3, respectively. These figures show that stations in Los Angeles have measured the highest peak concentrations. The oxides of nitrogen peak value in Los Angeles is an order of magnitude higher than in San Bernardino, the locality with the lowest peak value.

SEASONAL VARIATIONS OF NO_x CONCENTRATIONS

The concentrations of nitric oxide, the predominant oxide of nitrogen formed in high temperature combustion, are highest during the late fall and winter months when strong ground based inversions occur.

Nitric oxide is converted to nitrogen dioxide in the atmosphere. Therefore, the concentration of nitrogen dioxide depends not only on emissions of oxides of nitrogen and conditions of wind and inversion but also on sunlight intensity and the presence of organic compounds in the atmosphere.

The seasonal variations for NO_x and for NO₂ in five selected cities are shown in Figures 4 to 8. At the time that the maximum hourly averages of oxides of nitrogen were recorded in these cities, almost all of the oxides of nitrogen were in the form of nitric oxide. The seasonal pattern of nitric oxide, therefore, resembles that of oxides of nitrogen with the highest concentrations occurring in the fall and winter months.

The highest nitrogen dioxide concentrations also are measured during the winter months; however, high concentrations may also occur at other seasons of the year.

The concentrations of oxides of nitrogen and nitrogen dioxide shown in Figures 4 to 8 are the highest maximum hourly average that was measured during each month. The same patterns of seasonal variations shown in these figures are observed when the concentrations are expressed as: (1) monthly peak - the highest peak concentration observed during a month; (2) monthly average - the average of all hourly averages during a month; and (3) the monthly average of maximum hourly averages for each day of the month.

Table II

OXIDES OF NITROGEN
NUMBER AND PERCENT OF HOURS HAVING AVERAGE
CONCENTRATIONS IN THE SPECIFIED RANGES
SCAN, 1963-1964

	NUMBER OF HOURS MEASURED	NUMBER OF HOURS		PERCENT	
		0.25-0.49 ppm	0.50 ppm and Greater	0.25-0.49	0.50+
Los Angeles	13,970	1,957	601	14.0	4.3
Long Beach	14,126	2,278	901	16.1	6.4
Azusa ¹	12,550	39	-	0.3	-
San Francisco	12,748	1,510	179	11.8	1.4
Oakland	9,139	733	184	8.0	2.0
San Jose ²	5,042	644	93	12.8	1.8
San Diego	13,684	458	82	3.3	0.6
Sacramento	14,462	423	108	2.9	0.7
Stockton ³	7,020	88	1	1.3	a
Fresno	13,303	147	10	1.1	0.1
Bakersfield ⁴	3,958	44	-	1.1	-
Santa Barbara ⁵	7,177	20	-	0.3	-
Ventura ³	8,966	5	-	0.1	-
Orange	9,409	72	-	0.8	-
San Bernardino ⁶	9,868	3	-	a	-

¹ In 1964 January-November.

² In 1963 December only

³ In 1963 November and December only.

⁴ In 1963 April-December; in 1964 February, March and April.

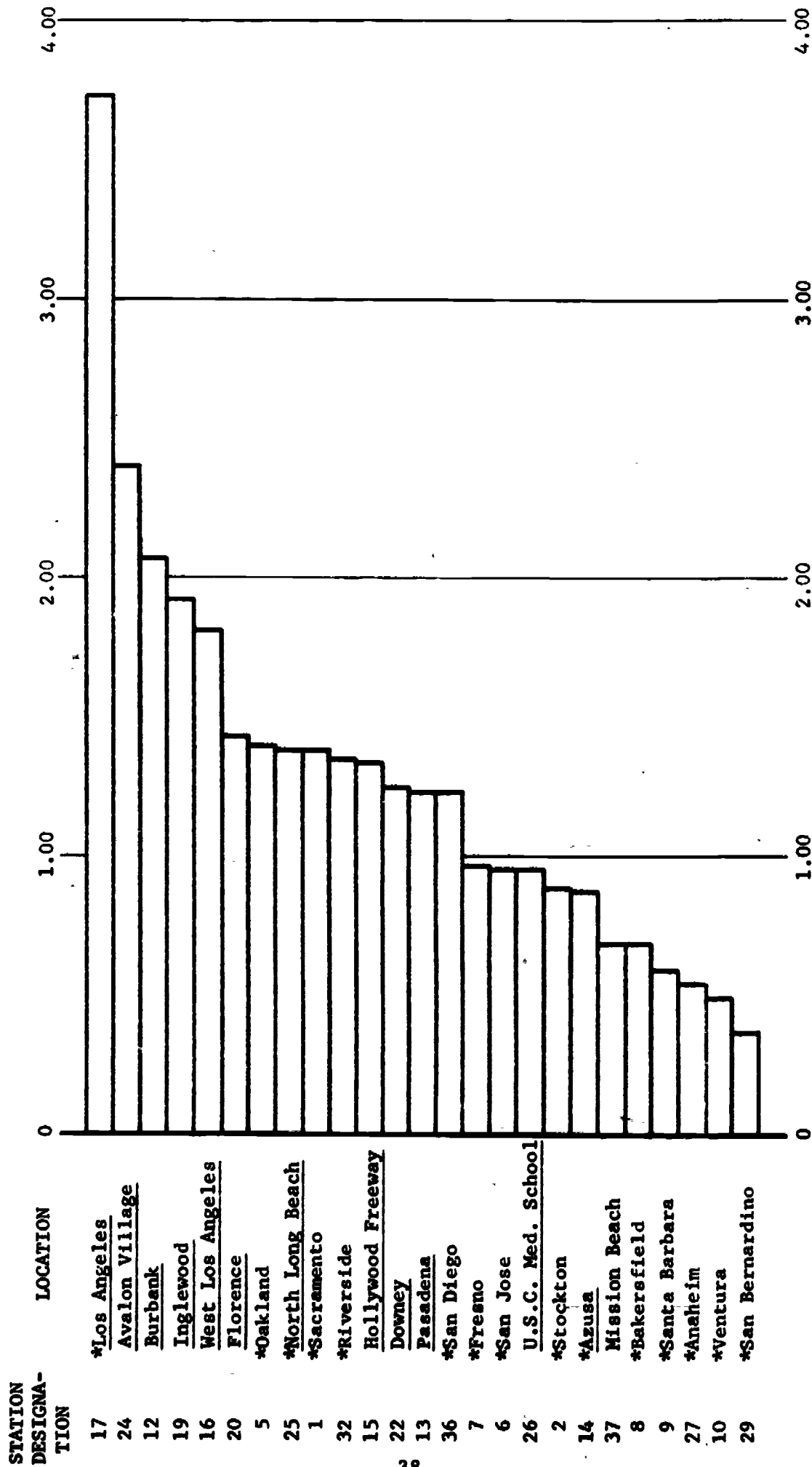
⁵ 1964 data only.

⁶ In 1963 January-October.

^a Less than 0.1.

Source: Los Angeles County Air Pollution Control District and
State of California Department of Public Health

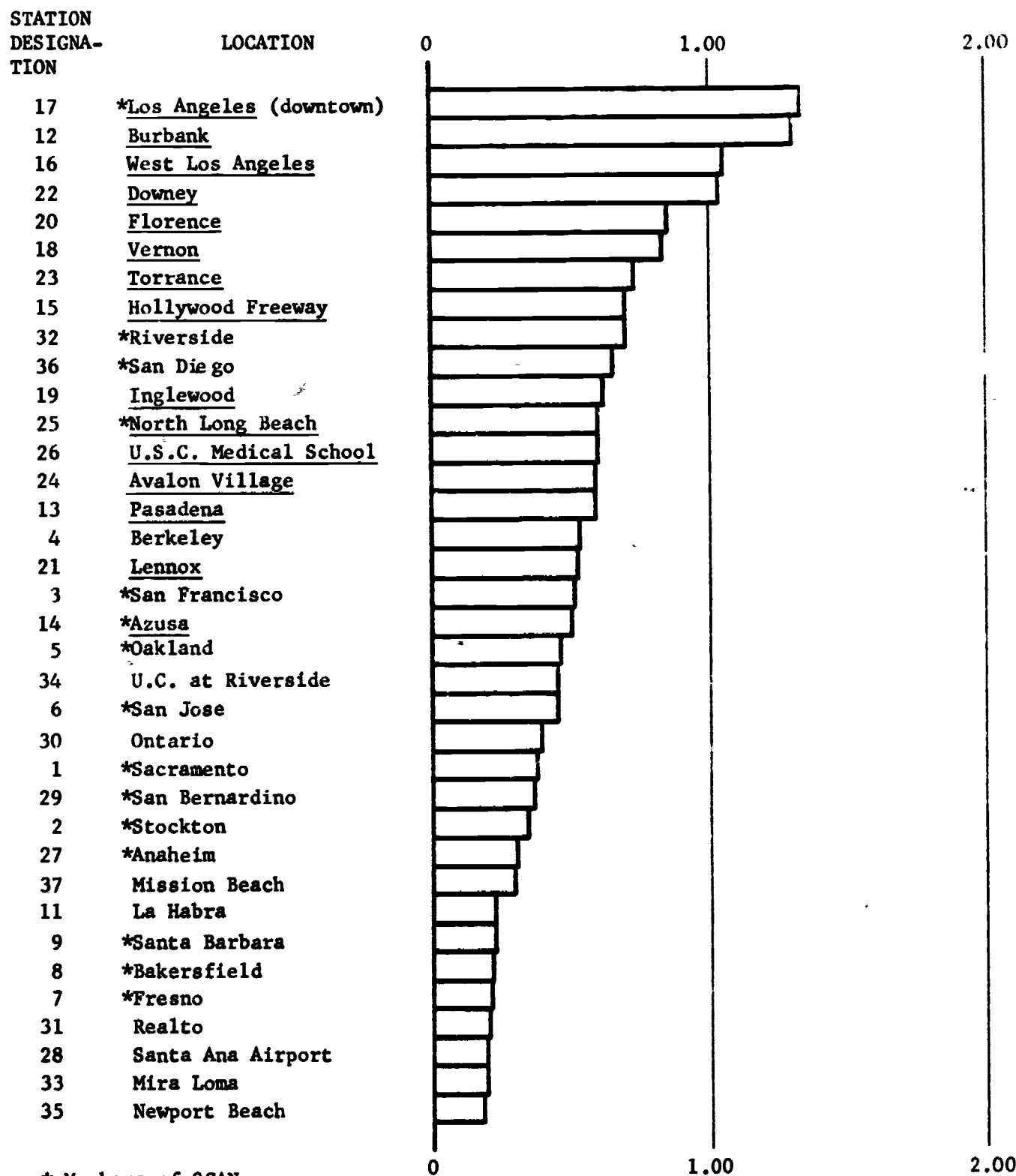
Figure 2
RECORD PEAK CONCENTRATIONS OF TOTAL OXIDES OF NITROGEN BY STATION (PPM)



* Members of SCAN
LAAPCD Stations are underlined

Figure 3

RECORD PEAK CONCENTRATION OF NITROGEN DIOXIDE (PPM)



* Members of SCAN
 LAAPCD Stations are underlined

Figure 4
MAXIMUM HOURLY AVERAGE CONCENTRATION BY MONTH
DOWNTOWN LOS ANGELES
1963-1964
(PPM)

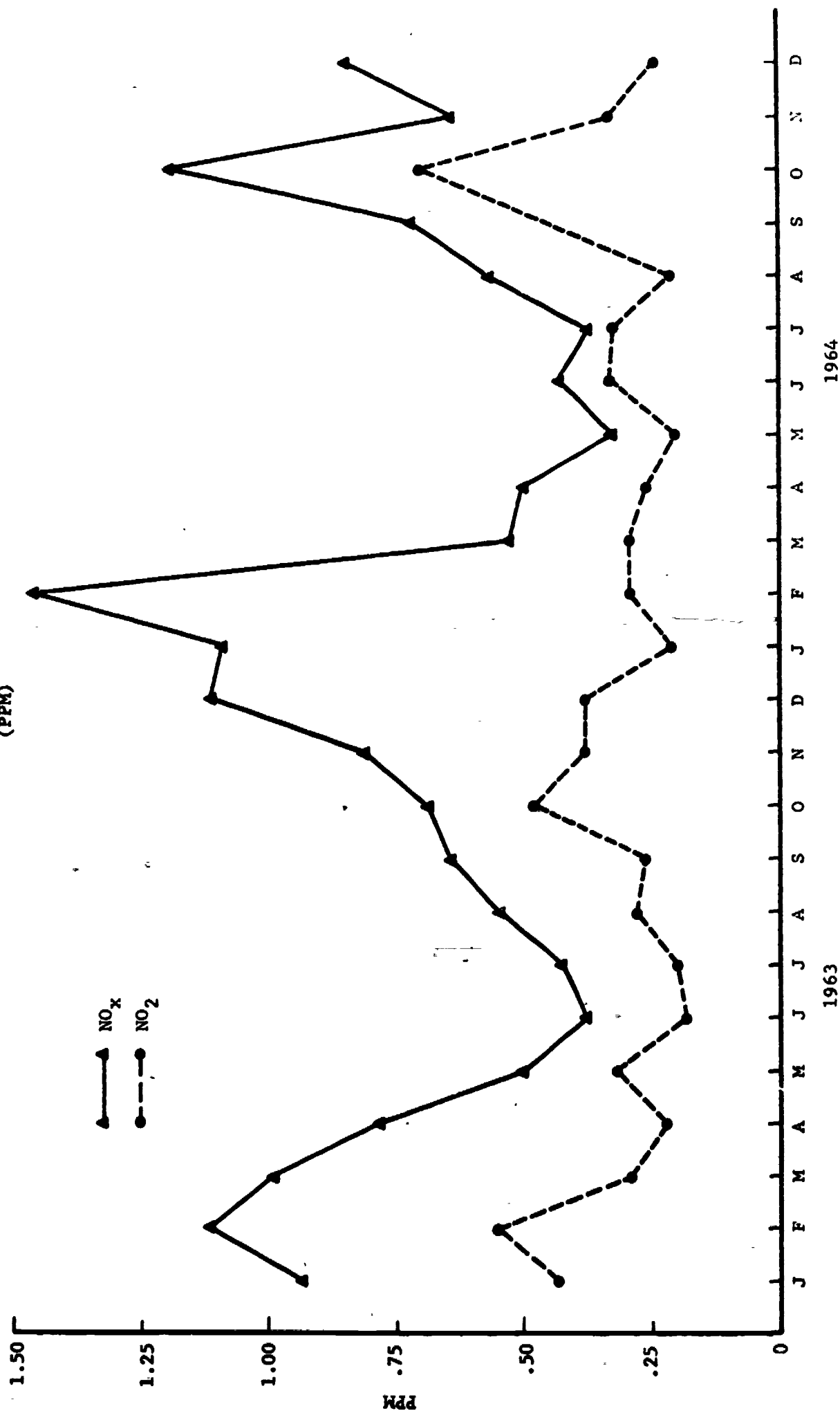


Figure 5
MAXIMUM HOURLY AVERAGE CONCENTRATION BY MONTH
OAKLAND
1963-1964
(PPM)

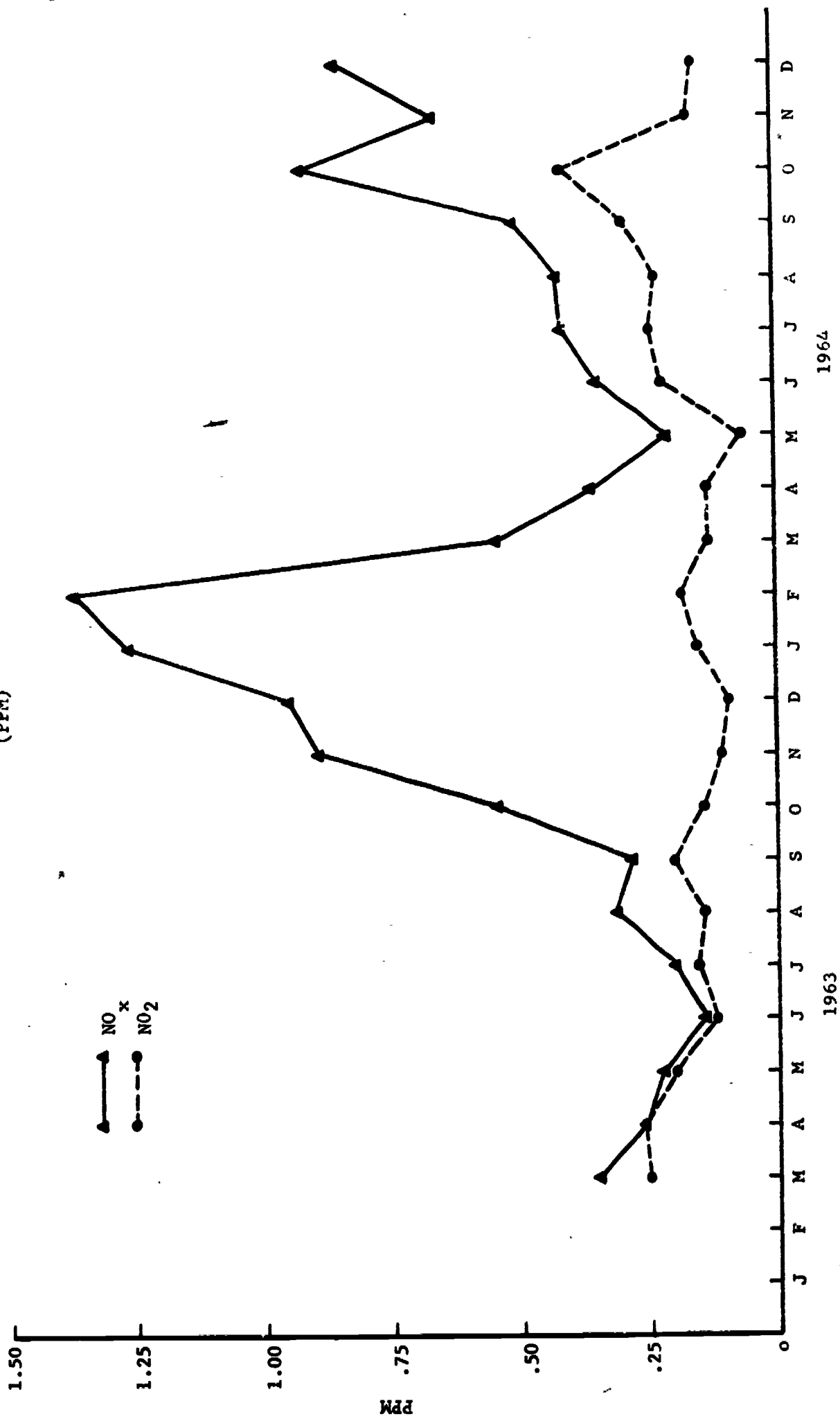
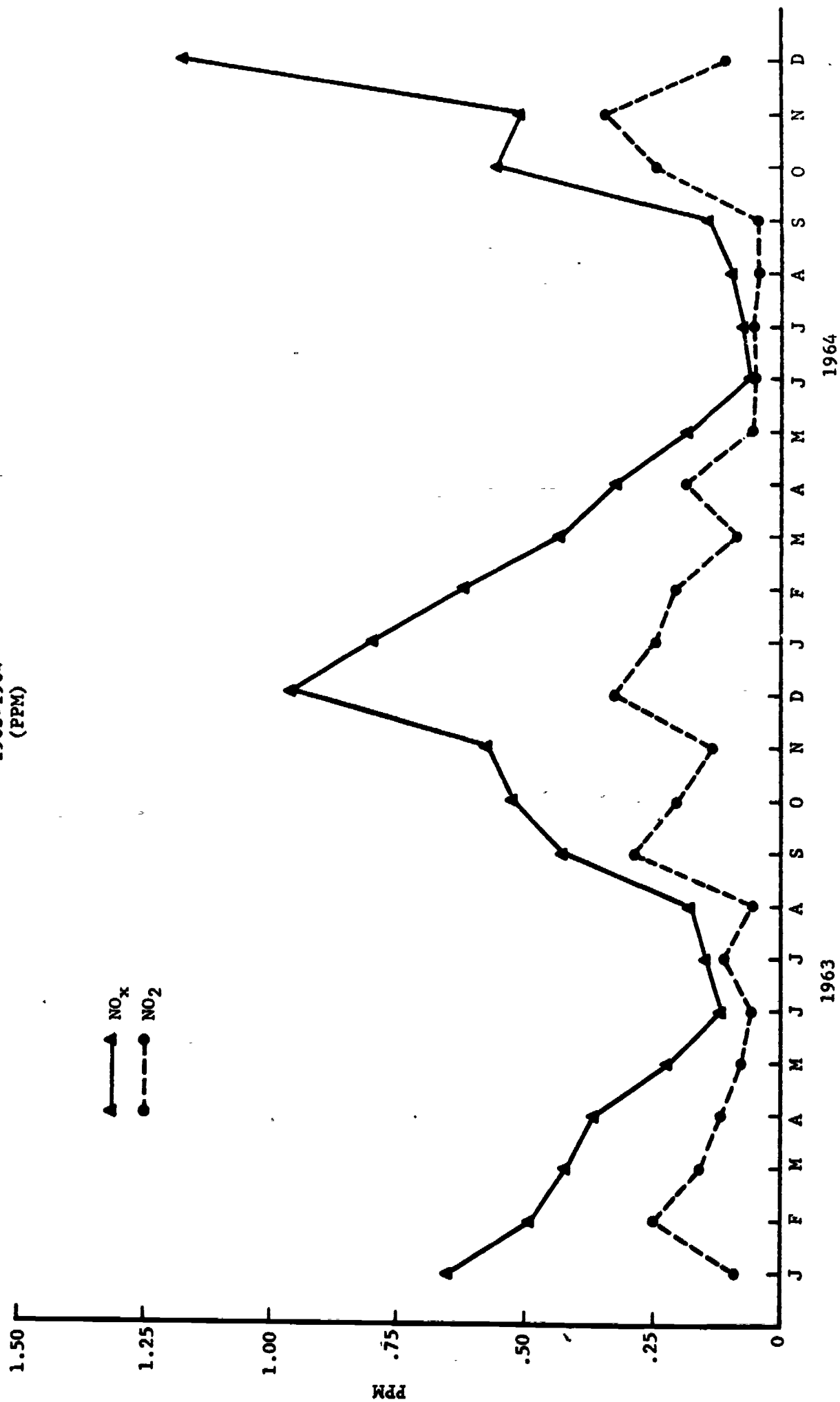


Figure 6
MAXIMUM HOURLY AVERAGE CONCENTRATION BY MONTH
SAN DIEGO
1963-1964
(PPM)



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Figure 7
MAXIMUM HOURLY AVERAGE CONCENTRATION BY MONTH
SACRAMENTO
1963-1964
(PPM)

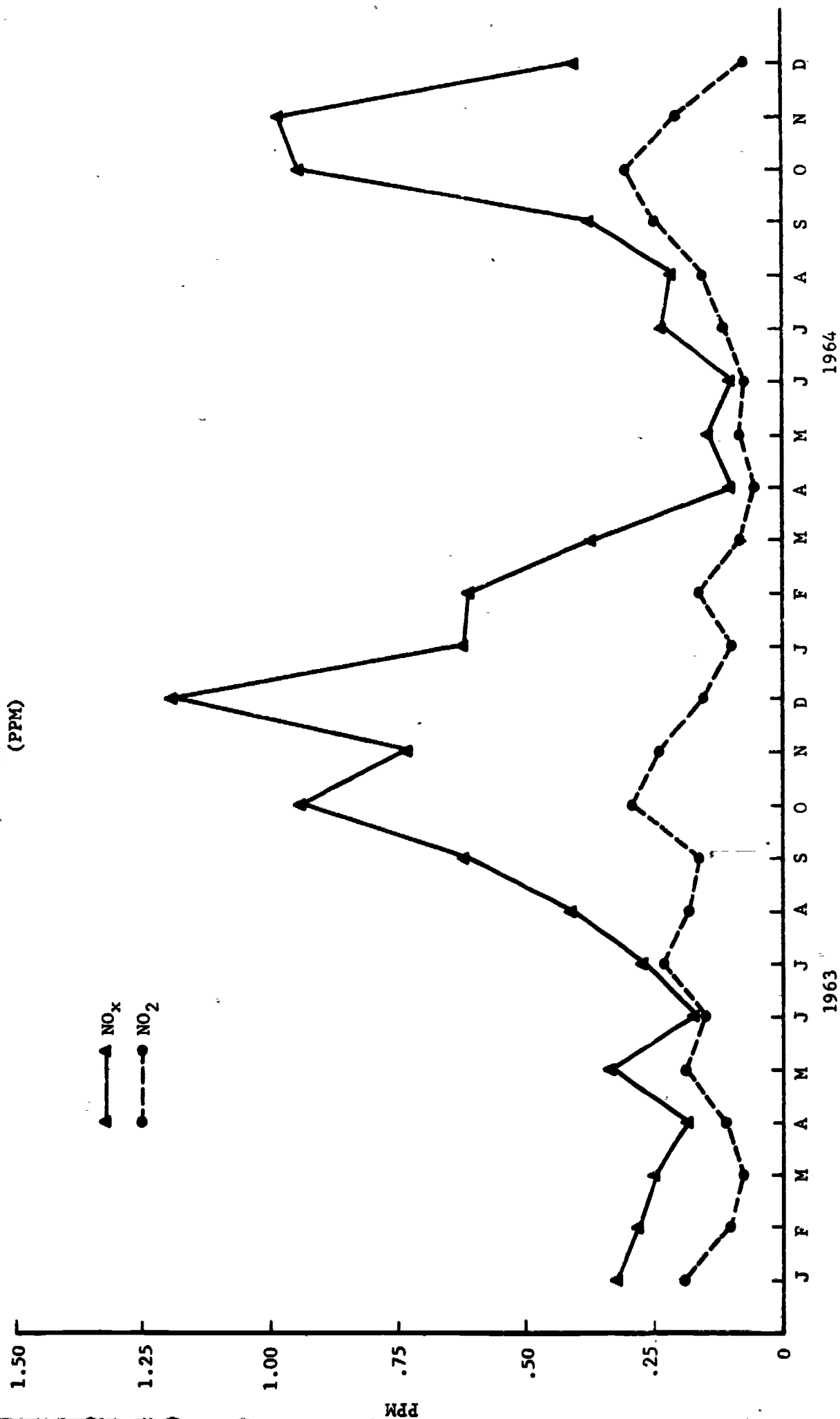
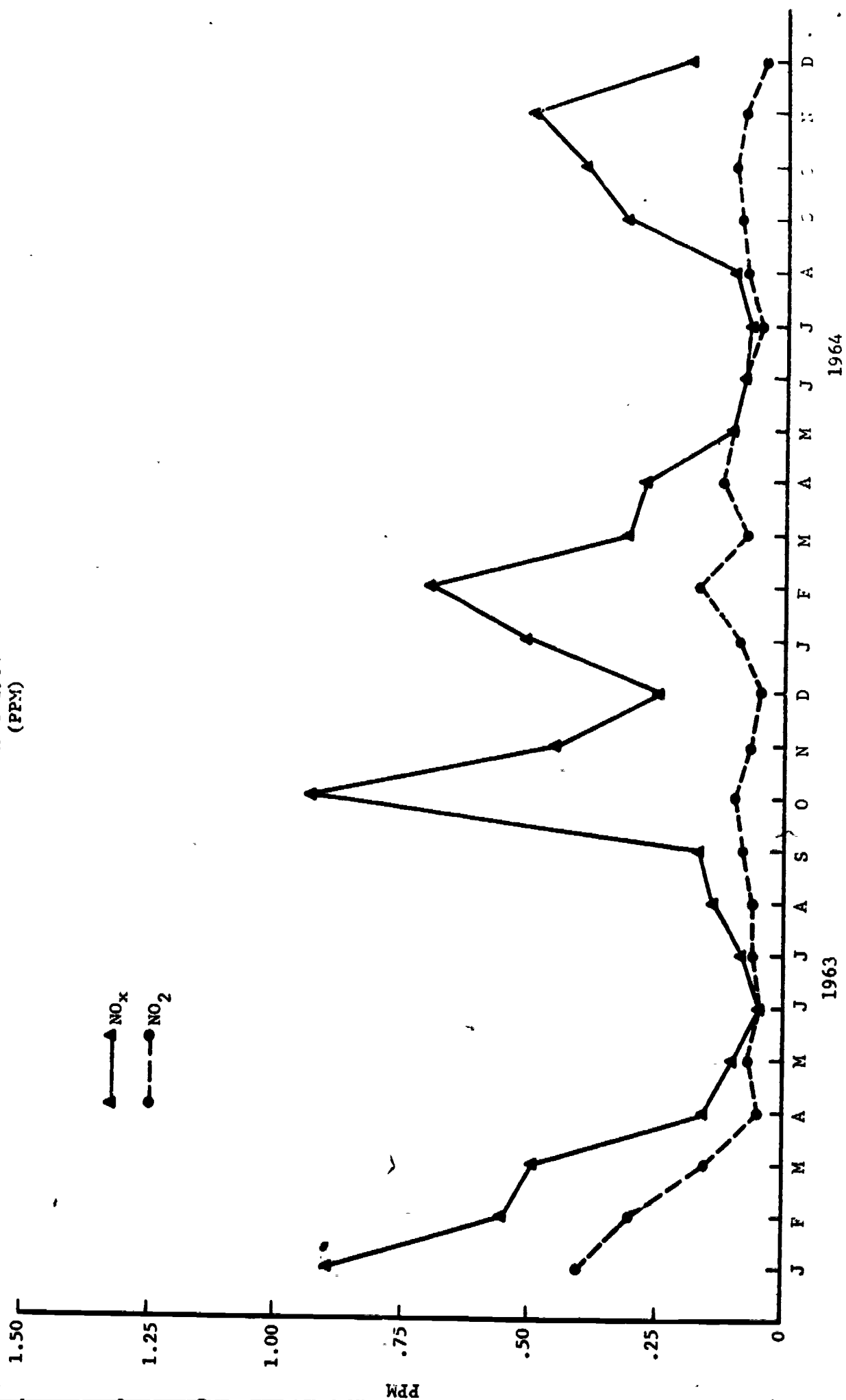


Figure 8
MAXIMUM HOURLY AVERAGE CONCENTRATION BY MONTH
FRESNO
1963-1964
(PPM)



DIURNAL VARIATIONS OF NO_x CONCENTRATIONS

The diurnal variations of oxides of nitrogen and nitrogen dioxide are illustrated in Figures 9 and 10 for three cities - Los Angeles, Oakland, and Sacramento. Concentrations are shown in Figure 9 for the month of February to represent the winter seasonal pattern and, in Figure 10, for September to represent fall.

The pattern for NO_x during both seasons is bimodal as the concentrations reach a peak during the morning hours and again during the late afternoon or evening hours. The morning peak begins to form at about 6:00 a.m., reaches a maximum at about 8:00 a.m., and then declines rapidly. The evening peak begins to form at about 5:00 p.m. and reaches a peak at about 8:00 p.m., although at times the concentration continues to rise during the evening hours.

The hours at which these peaks occur either coincide with, or take place shortly after, the hours of peak traffic conditions. The continual rise of NO_x during the evenings of some months may be ascribed to meteorological factors and to increased stationary source emissions during cold evenings.

Concentrations of NO₂ also reach a peak during the morning hours, following the NO_x morning peak by about an hour. This indicates that NO₂ is formed mainly from NO in the photochemical smog reaction during the daylight hours.

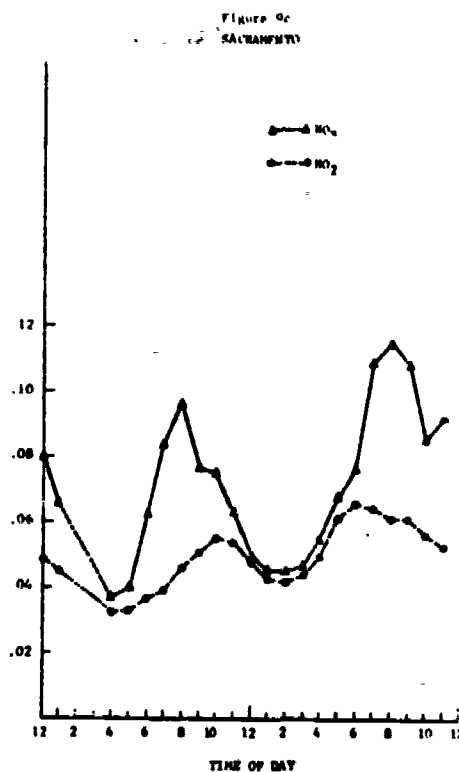
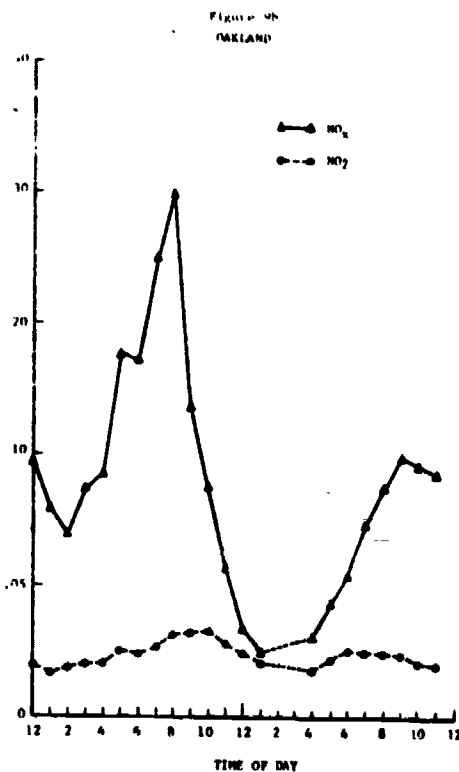
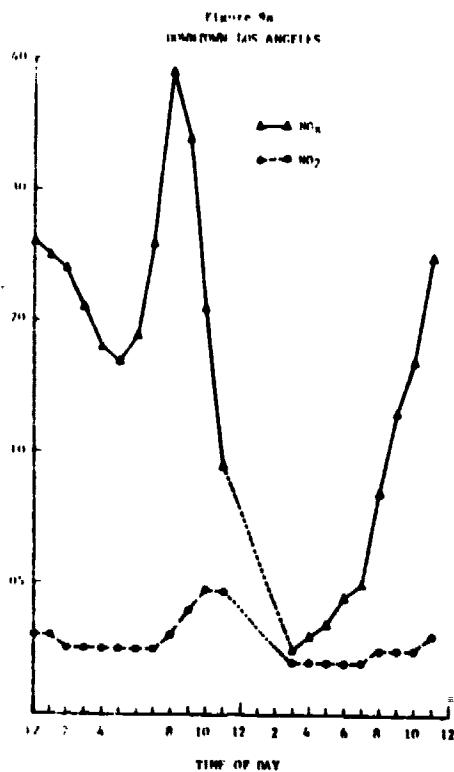
RELATIONSHIP BETWEEN ATMOSPHERIC CONCENTRATIONS OF NO_x AND OTHER POLLUTANTS

The air pollution photochemical reaction requires the presence of both oxides of nitrogen and hydrocarbons. Descriptions of this reaction, and predictions of the effects of control of oxides of nitrogen and hydrocarbons, are presented in a subsequent chapter. Necessary to the prediction of effects is a knowledge of the atmospheric levels of these contaminants.

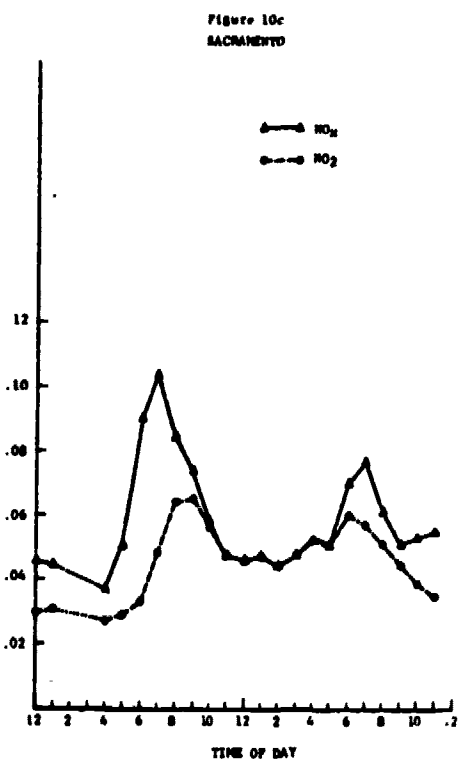
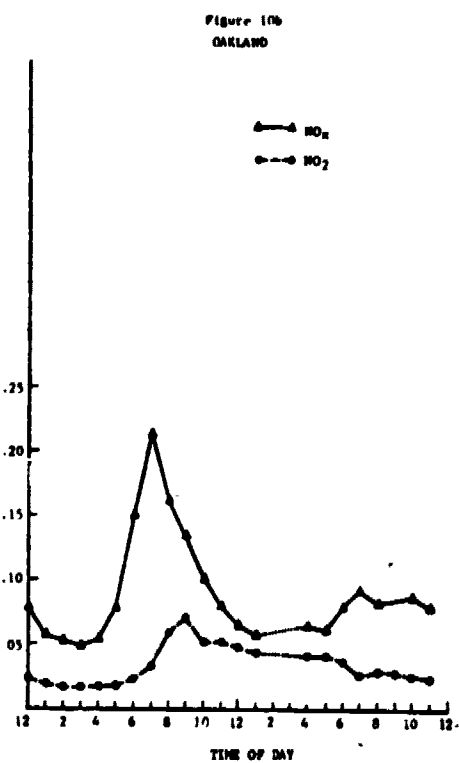
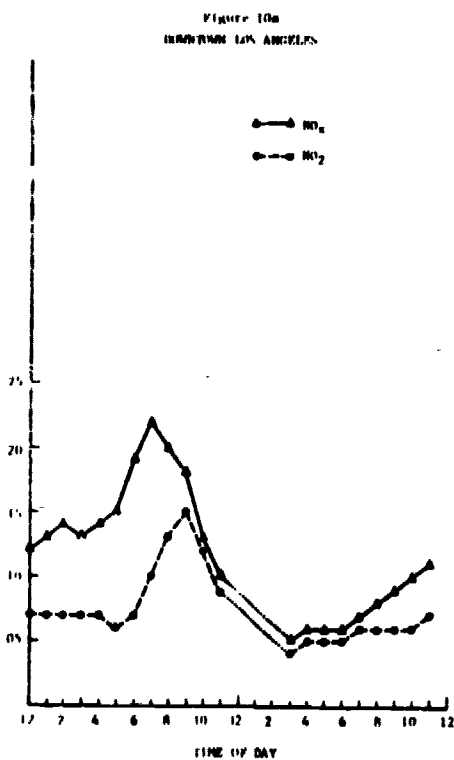
Continuous air monitoring for hydrocarbons began in downtown Los Angeles in 1962 by the Los Angeles County Air Pollution Control District. Flame Ionization (FI) analysers are used. These instruments measure the total hydrocarbon concentration in terms of carbon atoms. However, not all of the hydrocarbons measured by the FI instrument participate in the photochemical reaction. As a class, the olefins are the most reactive followed by the aromatics. Methane, ethane, propane, butanes, pentanes, acetylene, and benzene are not believed to be important in the reaction.

Analyses of specific atmospheric hydrocarbons have indicated that some non-reactive hydrocarbons may be from natural sources.⁽³⁾ Methane is

DIURNAL VARIATION
AVERAGE CONCENTRATION FOR EACH HOUR
FEBRUARY, 1964
(PPM)



DIURNAL VARIATION
AVERAGE CONCENTRATION FOR EACH HOUR
SEPTEMBER, 1964
(PPM)



the most abundant single hydrocarbon in the atmosphere and it may amount to 50 to 90% of the unreactive hydrocarbons.(4)

Concentrations of the primary pollutants - nitric oxide, carbon monoxide, and hydrocarbons - rise rapidly to a peak during the early morning hours of most smog days. The difference between the minimum and maximum values occurring during this period is an indication of the air pollutants recently added to the atmosphere.

The differences in concentrations expressed as delta (Δ) are shown in Table IV for the months of August, September, and October and in Table V for the months of November, December, and January. The values shown are the differences of the maximum and minimum 20 minute average concentrations between the hours of 5:00 a.m. and 9:00 a.m. in downtown Los Angeles. The days shown were selected on the basis of having a large difference of carbon monoxide and of being smog days.

Korth et al reported the concentrations of oxides of nitrogen and hydrocarbons which occurred on five days of severe eye irritation.(5) These were based on the highest five minute average for each day. Total hydrocarbon concentrations were corrected for background concentration which was the lowest value between midnight and the time of the peak. As shown in Table III the average hydrocarbon concentration was 5.2 ppm C; NO_x was 0.46 ppm; and the average ratio of hydrocarbons to NO_x was 11.1.

Table III

ATMOSPHERIC DATA

DATE	HYDROCARBON CONC. (PPM CARBON)	NO_x CONC. (PPM)	HC/ NO_x RATIO
8/7/62	3.2	0.32	10.0
8/8/62	8.0	0.59	13.5
8/9/62	3.0	0.32	9.4
8/14/62	5.0	0.45	11.1
9/20/62	7.0	0.62	11.3
Average	5.2	0.46	11.1

Source: Prepared from information in Reference 5.

The average ratios in the atmosphere are close to the ratios as emitted from motor vehicles shown in Tables IV and V. This signifies that motor vehicles are a major source of these pollutants in downtown Los Angeles during the morning hours.

On a daily basis the ratios, as well as the concentrations, vary widely. The hydrocarbon to oxides of nitrogen ratios range from 6.7 to 22.2 in the fall and from 7.8 to 25.0 during winter. The control of hydrocarbons

Table IV

RATIOS OF ATMOSPHERIC CONTAMINANT CONCENTRATIONS
LOS ANGELES STATION #1 - AUGUST, SEPTEMBER, OCTOBER
1962, 1963, 1964

(0500-0900) PST

DIFFERENTIAL (PPM)					RATIOS		
Date		Δ CO	Δ NO _x	Δ HC*	$\frac{\Delta\text{CO}}{\Delta\text{NO}_x}$	$\frac{\Delta\text{HC}}{\Delta\text{NO}_x}$	$\frac{\Delta\text{CO}}{\Delta\text{HC}}$
Monday	8- 6-62	9.0	.29	3.5	31	12.1	2.6
Tuesday	8- 7-62	10.0	.13	2.5	77	19.2	4.0
Wednesday	8- 8-62	15.5	.32	5.5	48	17.2	2.8
Friday	8-24-62	12.0	.33	3.0	36	9.1	4.0
Wednesday	9-19-62	14.5	.45	3.5	32	7.8	4.1
Thursday	9-20-62	13.5	.50	4.0	27	8.0	3.4
Friday	9-21-62	13.0	.46	4.0	28	8.7	3.3
Monday	10- 8-62	14.0	.23	4.0	61	17.4	3.5
Monday	10-29-62	20.0	.38	7.0	53	18.4	2.9
Tuesday	9-10-63	12.0	.27	2.5	44	9.3	4.8
Monday	10- 7-63	22.0	.64	8.5	34	13.3	2.6
Tuesday	10- 8-63	22.0	.37	8.0	59	21.6	2.8
Wednesday	10- 9-63	10.5	.27	3.5	39	13.0	3.0
Friday	10-11-63	11.0	.33	3.0	33	9.1	3.7
Monday	10-14-63	9.5	.38	4.5	25	11.8	2.1
Friday	10-18-63	9.0	.27	3.5	33	13.0	2.6
Tuesday	10-29-63	15.0	.45	5.5	33	12.2	2.7
Thursday	9- 3-64	21.5	.40	5.5	54	13.8	3.9
Thursday	9-10-64	13.5	.29	3.0	47	10.3	4.5
Thursday	9-24-64	21.0	.27	6.0	78	22.2	3.5
Wednesday	9-30-64	15.5	.29	4.0	53	13.8	3.9
Friday	10- 2-64	19.0	.52	3.5	37	6.7	5.4
Wednesday	10- 7-64	15.0	.36	5.5	42	15.3	2.7
Average		14.7	.36	4.5	43.5	13.2	3.4
Average Concentration in Exhaust		35,000	1,000	10,000	35	10	3.5

* in ppm Carbon

Table V

RATIOS OF ATMOSPHERIC CONTAMINANT CONCENTRATIONS
LOS ANGELES STATION #1 - NOVEMBER, DECEMBER, JANUARY
1962, 1963, 1964

(0500-0900) PST

DIFFERENTIAL (PPM)					RATIOS		
Date		Δ CO	Δ NO _x	Δ HC*	$\frac{\Delta\text{CO}}{\Delta\text{NO}_x}$	$\frac{\Delta\text{HC}}{\Delta\text{NO}_x}$	$\frac{\Delta\text{CO}}{\Delta\text{HC}}$
Thursday	11- 8-62	23.0	.55	7.0	42	12.7	3.3
Tuesday	11-20-62	21.0	.77	6.0	27	7.8	3.5
Monday	11-26-62	17.0	.24	6.0	71	25.0	2.8
Friday	11-30-62	20.0	.15	5.0	133	33.3	4.0
Monday	12- 3-62	19.0	.40	7.0	48	17.5	2.7
Wednesday	12- 5-62	26.0	.64	6.0	41	9.4	4.3
Thursday	12- 6-62	21.0	.50	5.5	42	11.0	3.8
Friday	12-21-62	21.0	.49	5.0	43	10.2	4.2
Tuesday	1-22-63	18.5	.41	3.5	45	8.5	5.3
Wednesday	1-23-63	16.5	.37	4.0	45	10.8	4.1
Monday	11-18-63	17.0	-	5.5	-	-	3.1
Friday	12-13-63	20.0	.67	7.0	30	10.4	2.9
Thursday	12-26-63	13.5	.31	5.0	44	16.1	2.7
Friday	12-27-63	19.0	.50	7.5	38	15.0	2.5
Friday	1- 3-64	26.5	.92	10.5	29	11.4	2.5
Monday	1- 6-64	16.0	.65	5.5	25	8.5	2.9
Monday	1-13-64	16.0	.65	-	25	-	-
Wednesday	1-15-64	15.5	.50	10.0	31	20.0	1.6
Thursday	1-16-64	19.0	.54	7.0	35	13.0	2.7
Tuesday	1-28-64	27.0	.92	-	29	-	-
Average		19.6	.54	6.3	43.3	14.2	3.3

Average
Concentration 35,000 1,000 10,000 35 10 3.5
in Exhaust

* As ppm Carbon

will lower the average ratio. But, on some days, the ratio may still be within these ranges although high ratios should occur less frequently.

Hydrocarbon concentrations are often measured and expressed on a molar (ppm HC) rather than on a carbon atom (ppm C) basis. Based on exhaust gas analysis, the average carbon number of exhaust hydrocarbon has been estimated approximately as 4.(6)(7) The average carbon number of crankcase and evaporative emissions are higher.(8)(9)(10) Assuming that the average carbon number of all motor vehicle emissions is 5 or 6, the average concentrations shown in Tables III, IV, and V, in terms of parts per million carbon atoms, are equivalent to approximately 1 ppm of hydrocarbon. The average NO_x concentration is about 0.5 ppm. The ratio of hydrocarbon on a molar basis to NO_x is, therefore, approximately 2:1.

Methane, ethane, propanes, butanes, pentanes, acetylene, and benzene constitute approximately 40 to 50% of the motor vehicle hydrocarbon emissions on a parts per million hydrocarbon basis.(6)(7)(8)(9)(10) If the remaining hydrocarbons (essentially the higher than five carbon atom paraffins, the olefins, and the other aromatics) are considered as "reactive" hydrocarbons, the ratio becomes about one part per million of reactive hydrocarbon per one part per million of oxides of nitrogen.

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Chapter VI

COLOR EFFECTS OF NITROGEN DIOXIDE IN THE ATMOSPHERE

Nitrogen dioxide (NO_2) absorbs light over the entire visible spectrum. The absorption coefficients of NO_2 have been measured by Dixon⁽¹⁾ in 1940 and by Hall and Blacet⁽²⁾ in 1952. At all wavelengths within the visible spectrum, the absorption of light by NO_2 obeys Beer's law as represented by the equation:

$$I_t = I_0 e^{-\sigma_\lambda C S} \quad (\text{eq. 1})$$

Where I_t = transmitted light intensity

I_0 = original intensity

σ_λ = extinction coefficient (2.3 x absorption coefficient)
for a given wavelength

C = concentration of NO_2

S = traversed path length

The extinction coefficients of NO_2 in terms of $\text{ppm}^{-1} \text{ mile}^{-1}$ and $\text{ppm}^{-1} \text{ Km}^{-1}$ for light of different wavelengths are shown in Table I.

Table I
EXTINCTION COEFFICIENT OF NO_2

WAVELENGTH, \AA	σ_λ , ($\text{PPM}^{-1} \text{ MILE}^{-1}$)	σ_λ , ($\text{PPM}^{-1} \text{ Km}^{-1}$)
4000	2.60	1.64
4500	2.07	1.31
5000	1.05	0.66
5500	0.47	0.30
6000	0.18	0.12
6500	0.062	0.039
7000	0.026	0.016

Source: Computed from the Summary in "Photochemistry of Air Pollution" Philip A. Leighton, Academic Press, 1961.

For an atmosphere containing NO_2 but free of aerosols, the extinction coefficient shown in Table I can be used directly to calculate the

transmitted light intensity. (Light is attenuated by molecular scattering, but this effect is very small compared to the light absorbed by NO_2 and can be ignored.)

Consider the case of an observer viewing a white object at a distance S miles through a nitrogen dioxide concentration C . At any given wavelength, the transmittance (fraction of the light transmitted, I_t/I_0) depends on the product of the concentration and the path length since σ_λ is constant. For example, the transmittance would be the same at $C = 1$ ppm and $S = 10$ miles as it would be at $C = 10$ ppm and $S = 1$ mile. The transmittance for several products of concentration and path length (CS) are summarized in Table II.

It can be seen from Table II and Figure 1 that the color from an equal-energy white object (i.e., one which radiates equal energy of all wavelengths) would be modified to contain proportionately more of the longer wavelength colors. At a CS of 0.1 ppm-mile, the modification is slight, and may not be apparent to the observer. This would be the case when the observer looks vertically at the blue sky through a thin, polluted layer. At 10 ppm-miles the transmittance of red (6500Å) is about 0.5, while it is almost zero for violet-green. Under this condition a distant white object or the horizon sky would appear reddish-brown. In between these extremes of concentration-distance combinations the white object would appear colored in shades ranging from pale yellow to reddish-brown.

Table II

TRANSMITTANCE ($\frac{I_t}{I_0}$) OF VISIBLE LIGHT BY NITROGEN DIOXIDE
IN AIR AT DIFFERENT (CS) VALUES

WAVELENGTH, Å	COLOR	0.1 PPM-MILE	1 PPM-MILE	3 PPM-MILES	10 PPM-MILES
4000	Violet	0.77	0.074	0.0004	5×10^{-12}
4500	Blue	0.82	0.126	0.002	1×10^{-9}
5000	Green	0.89	0.35	0.043	3×10^{-5}
5500	Yellow	0.96	0.63	0.24	0.010
6000	Orange-red	0.98	0.84	0.58	0.17
6500	Red	0.99	0.94	0.83	0.54
7000	Red	0.99+	0.98	0.93	0.77

Source: Reference (3). Values for 0.1 ppm NO_2 and 1 mile path length are computed, using the extinction coefficients in Table I.

In an atmosphere containing NO_2 and aerosols the situation is more complicated. The transmitted light from an object would be further

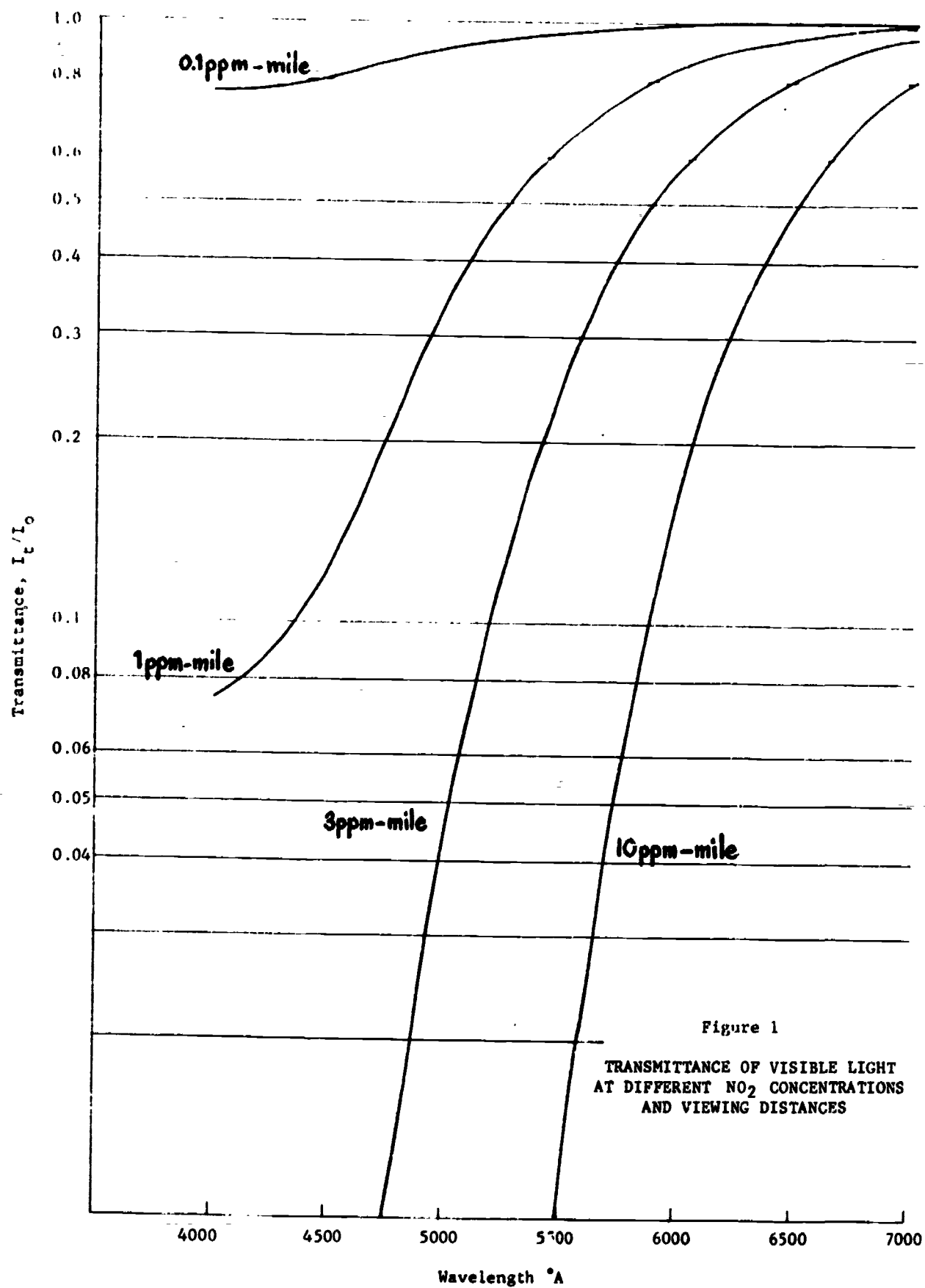


Figure 1
TRANSMITTANCE OF VISIBLE LIGHT
AT DIFFERENT NO_2 CONCENTRATIONS
AND VIEWING DISTANCES

attenuated due to light scattering by the aerosols. The total attenuation coefficient becomes $\sigma_a C + \sigma_s$ where σ_s is the scattering coefficient of the aerosols. The transmitted luminance, B_t , of an object becomes

$$B_t = B_0 e^{-(\sigma_a C + \sigma_s) S} \quad (\text{eq. 2})$$

where B_0 = the original luminance of the object. Augmenting B_t is that part of the scattered air-light which is in the direction of the observer. This scattered luminance is:

$$B_s = A \left(\frac{\sigma_s}{\sigma_a C + \sigma_s} \right) [1 - e^{-(\sigma_a C + \sigma_s) S}] \quad (\text{eq. 3})$$

where A is the volume scattering factor and is independent of wavelength. The apparent luminance of any object to the observer at any distance is the sum of $B_t + B_s$. Since σ_a varies with wavelength, B_t and B_s will also vary with wavelength.

The fractional reduction in transmitted luminance due to absorption by NO_2 alone is the same whether aerosols are present or not. This is shown as follows:

In the absence of NO_2 , ($C = 0$)

$$B_{t(C=0)} = B_0 e^{-\sigma_s S} \quad (\text{eq. 4})$$

The transmitted luminance with NO_2 present, relative to that with NO_2 absent, is therefore:

$$\frac{B_t}{B_{t(C=0)}} = \frac{e^{-(\sigma_a C + \sigma_s) S}}{e^{-\sigma_s S}} = e^{-\sigma_a C S} \quad (\text{eq. 5})$$

which is the transmittance through NO_2 (equation 1). This ratio approaches zero as S approaches infinity.

In the absence of NO_2 , the scattered luminance becomes

$$B_{s(C=0)} = A (1 - e^{-\sigma_s S}) \quad (\text{eq. 6})$$

The scattered luminance at a given aerosol concentration (for a given σ_s) with the presence of NO_2 , relative to that in the absence of NO_2 , is then:

$$\frac{B_s}{B_s(c=0)} = \left(\frac{\sigma_s}{\sigma_a c + \sigma_s} \right) \left[\frac{1 - e^{-(\sigma_a c + \sigma_s)S}}{1 - e^{-\sigma_s S}} \right] \quad (\text{eq. 7})$$

The limit of this ratio as S approaches infinity is

$$\frac{\sigma_s}{\sigma_a c + \sigma_s}$$

Consider now the case of an observer viewing the horizon sky, and assume that the distance S approaches infinity. Under this condition the transmitted luminance becomes zero and the sky luminance is entirely due to light scattering. When the transmitted luminance of a distant object is negligible compared to its scattered luminance, the appearance of the object would be similarly affected as the horizon sky. In such cases, the spectral energy that the eye receives is proportional to $\frac{\sigma_s}{\sigma_a c + \sigma_s}$. When C is 0, the ratio is unity. With increasing NO_2 concentrations, the ratio and consequently the spectral energy received by the eye decreases. A short wavelength light which has a high σ_a will be attenuated more than light of longer wavelengths. If σ_s becomes larger, as in the case of high aerosol concentration, the ratio will become closer to unity and the effect of the NO_2 absorption of light will become obscured.

Dr. J. Raymond Hodgkinson,⁽⁴⁾ consultant to the U.S. Public Health Service, calculated the effect of NO_2 and of aerosols on the horizon sky and distant white surfaces at selected concentrations. He estimated that with unit density and $\frac{1}{2}$ micron diameter aerosols at concentrations of 4800, 1200, and 300 particles per cubic centimeter, the aerosol scattering coefficient σ_s was 2, 0.5, and 0.125 Km^{-1} , respectively. Table III and Figure 2, showing different values of $\frac{\sigma_s}{\sigma_a c + \sigma_s}$ at different concentrations of NO_2 and aerosols are based on Hodgkinson's approach. A σ_s value of 0.06 mile^{-1} would correspond to an atmosphere containing almost no aerosols.

Dr. Philip A. Leighton⁽⁵⁾ has also calculated the optical effects of NO_2 in an atmosphere containing aerosols. He illustrated, as a specific example, an observer viewing green trees, which reflect light in the region of 5000-5500 \AA , at a distance of three miles, using a scattering coefficient of .75 mile^{-1} . Under these conditions, in the absence of NO_2 , the transmittance, $\frac{I_t}{I_0} = e^{-(.75)(3)} = 0.1$. The extinction coefficient

of nitrogen dioxide at green wavelength is approximately 0.75 $\text{ppm}^{-1} \text{mile}^{-1}$ (see Table I). At a concentration of 1 ppm of NO_2 and in the

Table III

ATTENUATION IN SPECTRAL LUMINANCE OF
HORIZON SKY AT DIFFERENT NO₂-
AEROSOL CONCENTRATIONS

$$\left(\frac{\sigma_s}{\sigma_{\lambda c} + \sigma_s} \right)$$

ATTENUATION COEFFICIENT	$\sigma_s = 3.2 \text{ MILE}^{-1}$			$\sigma_s = 0.8 \text{ MILE}^{-1}$		$\sigma_s = 0.4 \text{ MILE}^{-1}$		
Wavelength \AA	0.2 ppm	1 ppm	2 ppm	0.2 ppm		0.5 ppm	1 ppm	2 ppm
4000	0.86	0.55	0.38	0.60		0.24	0.13	0.071
4500	0.88	0.60	0.43	0.66		0.28	0.16	0.088
5000	0.94	0.75	0.60	0.79		0.43	0.28	0.16
5500	0.97	0.87	0.77	0.89		0.63	0.46	0.30
6000	0.99	0.94	0.89	0.95		0.82	0.69	0.53
6500	0.996	0.98	0.96	0.98		0.93	0.87	0.76
7000	0.998	0.99	0.98	0.99		0.97	0.94	0.88

presence of aerosols the transmittance becomes

$$\frac{I_t}{I_0} = e^{-(.75 + .75)(3)} = 0.01$$

Thus, the addition of 1 ppm of NO₂ causes a tenfold reduction in the transmittance of the green light. To maintain the same transmittance when 1 ppm of NO₂ is present, the path length must be reduced from 3 to 1.5 miles.

Leighton has also shown that the apparent green object brightness - that is, the ratio of the transmitted light intensity to the forward scattered light intensity - would be diminished by a factor of 5.6 if 1 ppm of NO₂ is added to the atmosphere where the aerosol attenuation coefficient is 0.75 mile⁻¹. To maintain the same apparent brightness the path length must be reduced from 3 to 1.2 miles.

Similarly, he calculated that, to maintain the same contrast, the path length must be reduced from 3 to 1.9 miles.

For a case of trees with a tenfold difference in brightness, he estimated that the apparent brightness ratio would be 1.72 when viewed through three miles of atmosphere containing aerosols having $\sigma_s = .75 \text{ mile}^{-1}$. The addition of 1 ppm of NO₂ would reduce the brightness ratio to 1.14. In this case with the addition of NO₂, the same apparent brightness cannot be attained at any path length.

DISCUSSION

Nitrogen dioxide is highly colored. In the atmosphere it will reduce the brightness and the contrast of distant objects as well as to cause the horizon sky and white objects to have a color ranging from pale yellow to reddish-brown. These colors have been described as similar to colors of whiskey, tea or cola depending on the NO_2 concentration, viewing distance, and aerosol concentration. The effect of aerosols is to mask the coloration effect of NO_2 , and to reduce visibility, contrast, and brightness of distant objects.

It cannot be stated at this time the definite aerosol and NO_2 concentrations at which the coloration effect of NO_2 would be readily noticeable and objectionable to most people. Under conditions where the transmitted luminance of an object is negligible compared to its scattered luminance, attenuation by NO_2 and aerosol is approximately proportional to the ratio $\frac{\sigma_s}{\sigma_a C + \sigma_s}$. From Figure 2, it can be seen that when 0.2 ppm NO_2 is present on days of poor visibility (i.e., aerosol scattering coefficient, σ_s of 3.2 mile^{-1}) the color of horizon sky and distant white objects is modified only slightly. At 2 ppm NO_2 on days of good visibility, say a visual range of approximately 10 miles, (corresponding to aerosol concentration 600 particles/cc, $\sigma_s = 0.4 \text{ mile}^{-1}$) the horizon sky and distant white objects would appear brownish. The level where the coloration effect is first noticeable is between these two curves, perhaps at 0.5 ppm NO_2 on days of 10 miles visibility.* This effect is represented in Figure 2 by the curve for $\sigma_s = 0.4 \text{ mile}^{-1}$, 0.5 ppm NO_2 .

If, however, aerosol concentrations were minimized through control of hydrocarbons, other organic compounds or particulate matter, the coloration effect of 0.5 ppm NO_2 on objects 10 miles distant would be more pronounced. To prevent the increase of coloration effect caused by a reduction of aerosol, a corresponding decrease in NO_2 concentration would be required. This can be illustrated as follows: When the scattered luminance predominates, the attenuation of a given wavelength is represented by $\frac{\sigma_s}{\sigma_a C + \sigma_s}$. The ratio will remain constant if both σ_s and C are reduced by the same factor. If the aerosol concentration is halved, the NO_2 concentration will also have to be halved.

In the absence of aerosol, the ratio $\frac{\sigma_s}{\sigma_a C + \sigma_s}$ equals zero, scattered luminance equals zero, and the coloration effect is one of attenuation by NO_2 absorption alone. In this case the allowable concentration for NO_2 would be very low. Figure 1 shows that at 0.3 ppm NO_2 for a 10 mile viewing distance ($C = 3 \text{ ppm}$) very little blue and green would come through. The effect of 0.01 ppm NO_2 on distant objects being viewed through a distance of 10 miles, on the other hand, is very slight and would not be apparent to an observer. The acceptable ambient NO_2

* "Visibility" is defined as the maximum distance at which a reference object can be seen. "Viewing distance" is simply the distance between the viewer and the object.

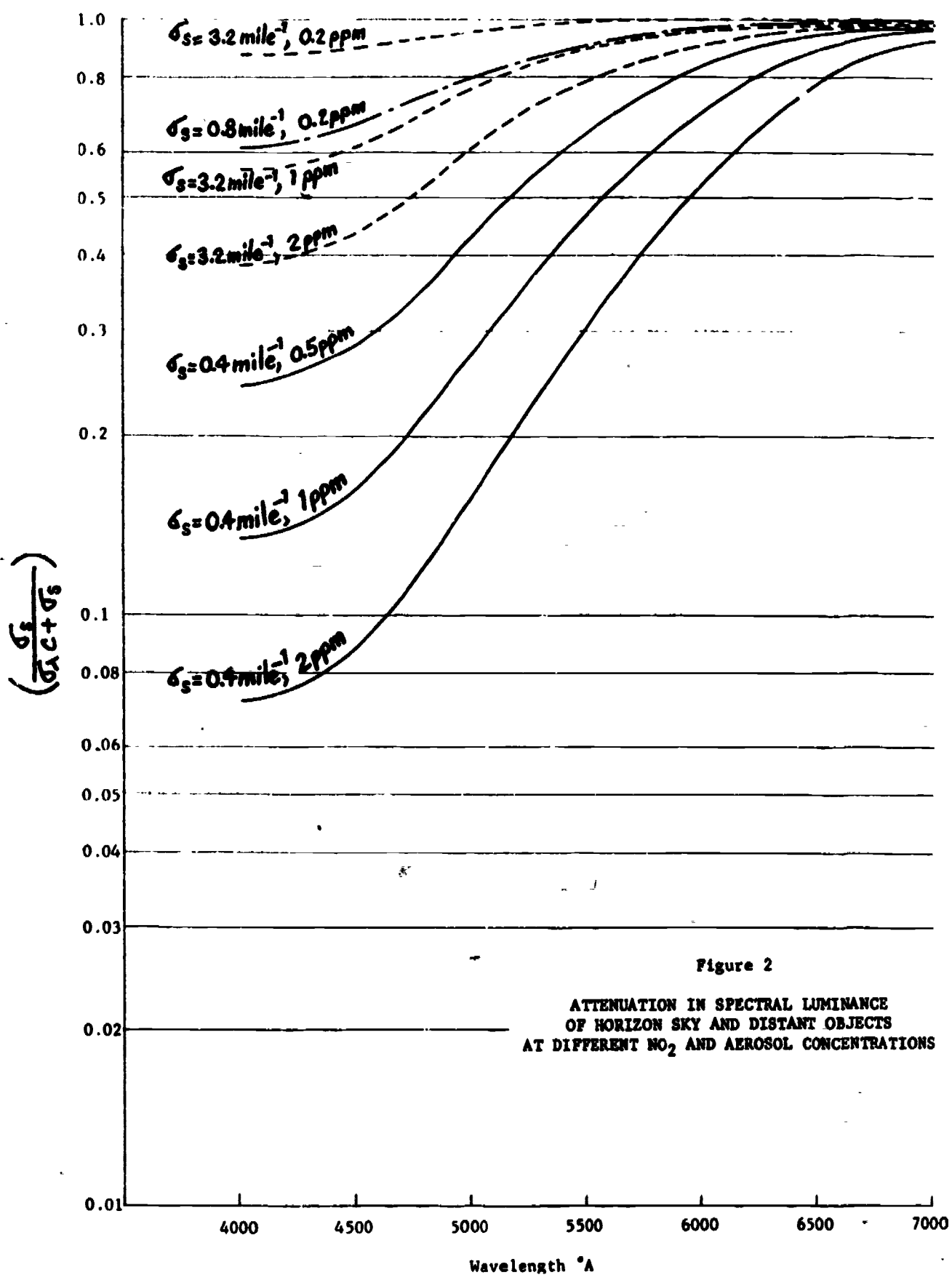


Figure 2
ATTENUATION IN SPECTRAL LUMINANCE
OF HORIZON SKY AND DISTANT OBJECTS
AT DIFFERENT NO_2 AND AEROSOL CONCENTRATIONS

concentration in the absence of aerosol with respect to coloration effect must therefore lie between 0.01 and 0.3 ppm for a path length of ten miles.

Assuming that the effect on the horizon sky due to 0.5 ppm of NO₂, under conditions where the visual range is 10 miles, is the criterion for an ambient air quality standard, the concentration of NO₂ which yields the same effect in the absence of aerosols can be evaluated. The combined effect of NO₂ and aerosols on each wavelength is represented by the expression $\frac{\sigma_s}{\sigma_a C + \sigma_s}$ for that wavelength. As suggested by Dr. Leighton, by setting the transmitted luminance in the absence of aerosols equal to this expression, the corresponding (C)(S) can be calculated. This would be the combination of NO₂ concentration and viewing distance which would produce the accepted effects in an aerosol-free environment. For example, at 5000Å (green), the value of $\frac{\sigma_s}{\sigma_a C + \sigma_s}$ is 0.43 under the specified criterion. In the absence of aerosol, $B_t/B_0 (C = 0) = e^{-\sigma_s S}$ the corresponding CS value is 0.8 ppm - mile.

The $\frac{\sigma_s}{\sigma_a C + \sigma_s}$ values and the corresponding CS values for other wavelengths are tabulated in Table IV. They range from 0.55 for 4000Å to 1.50 for 7000Å with an average of 1.0 ppm - mile. For a viewing distance of 10 miles, the ambient air concentration of NO₂ would have to be maintained at 0.1 ppm or less to meet the criterion.

Table IV

ARBITRARY ACCEPTABLE LIMIT* AND CS PRODUCT
WHICH YIELDS THIS LIMIT THROUGH NO₂ ABSORPTION

Å°	$\frac{\sigma_s}{\sigma_a C + \sigma_s}$ FROM (TABLE III)	CS**
4000	0.24	0.55
4500	0.28	0.62
5000	0.43	0.80
5500	0.63	1.00
6000	0.82	1.10
6500	0.93	1.30
7000	0.97	1.50

* The acceptable limit for a given wavelength is arbitrarily selected as the effect on that wavelength by scattering, with S = 10 miles, C = 0.5 ppm NO₂, $\sigma_s = 0.4$ mile⁻¹

** Calculated by equating $\frac{\sigma_s}{\sigma_a C + \sigma_s}$ to $e^{-\sigma_a C S}$

SUMMARY

The coloration effect of NO_2 in the atmosphere depends on NO_2 concentration, viewing distance, and aerosol concentration. The effect of 0.5 ppm NO_2 , with a viewing distance of 10 miles, is postulated to be acceptable on days of 10 mile visibility. In an aerosol-free atmosphere, with the same viewing distance of 10 miles, the acceptable NO_2 concentration is about 0.1 ppm. In reality, an aerosol-free atmosphere does not occur in metropolitan areas, and a visibility of 20 miles would represent a reasonable goal for atmospheric clarity. On such days, the acceptable NO_2 concentration would be about 0.25 ppm.

ACKNOWLEDGMENT

The Department gratefully acknowledges the assistance and information provided by Dr. Philip A. Leighton, Professor Emeritus of Stanford University; the Division of Air Pollution, U.S. Public Health Service; and Dr. J. Raymond Hodkinson, Head, Department of Physics, Virginia State College, Petersburg, Virginia.

The Department has taken freely the information provided by these scientists and is fully responsible for the conclusions herein.

Dr. Hodkinson's manuscript, "Calculations of Color and Visibility in Urban Atmospheres", is in preparation for submission to the International Journal of Water and Air Pollution. Dr. Leighton's calculations and derivations are on file in the Bureau of Air Sanitation, California Department of Public Health, 2151 Berkeley Way, Berkeley, California.

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Chapter VII

PHYTOTOXICITY OF NITROGEN DIOXIDE

Nitrogen dioxide is a phytotoxic substance. It can cause vegetation damage which is distinct from the damage caused by photochemical air pollution in general. There are few studies of the phytotoxic effects of nitrogen oxides. What is available has been reviewed by Dr. O. C. Taylor, Associate Horticulturist, Air Pollution Research Center* at Riverside, California. The following is a summary of his review.

"The phytotoxic effects of nitrogen oxides, aside from their role as a precursor of oxidizing air pollutants, have not been studied extensively. This lack of interest in nitrogen oxides as phytotoxicants has resulted from reliable reports of plant damage only from concentrations well above those measured in the atmosphere. According to Thomas,⁽¹⁾ the levels of nitrogen oxide in the atmosphere will probably always be too low to cause plant damage. Benedict and Breen⁽²⁾ found that the most sensitive weed species used in their experiments required 20 ppm NO_2 to cause damage. Pinto bean leaves require only 3 ppm NO_2 for 4 to 8 hours to develop damage.⁽³⁾⁽⁴⁾ This damage was reported to resemble that caused by exposure to sulfur dioxide.

"Bush et al.⁽⁵⁾ have reported an 'atypical' smog damage which was thought to be caused by low concentrations of nitrogen dioxide. This chlorosis of the lower leaves of Nicotiana glutinosa is different from the typical 'smog' or 'oxidant' type of plant damage. They suggest that long exposure to concentrations in the vicinity of parts per ten million of air may be causing this damage.

"A manuscript presently being prepared for presentation for publication in the Journal of Plant Physiology⁽⁶⁾ describes experiments with bean and tomato plants exposed to nitrogen dioxide at concentrations below 0.5 ppm. In these experiments young tomato and bean seedlings were exposed continuously to 0.5 ppm or less of NO_2 for 12 to 19 days. In each instance, significant growth reduction, expressed as fresh and dry weight, occurred with no visible lesions of damage. Leaves of tomato exposed to the NO_2 tended to curve or cup downward and a noticeably darker green appearance was noted.

"Exposure of bean, tomato, and Nicotiana glutinosa plants to 2.5 ppm NO_2 for 7 hours or more caused collapsed white lesions on the leaves resembling damage by SO_2 as described by Middleton et al.⁽⁴⁾ The

*University of California

lesions did not occur at concentrations less than 2.5 ppm even though the fumigations were extended to as long as three days.

"From the limited amount of information available it would appear that acute symptoms of damage to sensitive plants occur only with concentrations of NO_2 above 2 to 2.5 ppm. There is also sufficient evidence to suggest that concentrations of NO_2 well below 1 ppm may cause significant growth suppression, chlorosis, and perhaps premature abscissions of leaves."

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Chapter VIII

PHOTOCHEMICAL EFFECTS OF NITROGEN OXIDES

Nitrogen oxides comprise one of the two groups of chemical compounds which are the raw materials for the production of photochemical smog. The other group consists of organic compounds. Hydrocarbons are believed to be the most important organic compounds in the Los Angeles atmosphere because of the reactivity of many of this class of compounds.

There is general agreement that photochemical smog would be eliminated if either the nitrogen oxides or organic compounds were completely controlled.

Control of hydrocarbon emissions to the atmosphere was started in the early 1950's shortly after the original discovery of the photochemical nature of Los Angeles smog by Dr. A. J. Haagen-Smit and his co-workers. In compliance with regulations of the Los Angeles County Air Pollution Control District, the petroleum refining industry was required to limit discharges from manufacturing operations and, by 1955, had reduced hydrocarbon losses by hundreds of tons per day.

A few years later the District adopted a rule to augment hydrocarbon control through regulation of the olefin content of gasoline. This action was directed at selectively reducing the emission of a highly reactive class of hydrocarbons from operations involving the production, distribution, and consumption of gasoline.

The first motor vehicle emission standards established in 1959 and 1960 by the California Department of Public Health required a large reduction in hydrocarbon emissions from motor vehicle exhausts and crankcase vents. Actual control of crankcase hydrocarbon emissions began in 1960, and, in late 1965, exhaust hydrocarbon control will begin on new cars sold in California.

During the period from the early 1950's to 1959, the emphasis on control of motor vehicle emissions was placed on hydrocarbons rather than both hydrocarbons and nitrogen oxides. This attitude reflected the stage of knowledge of the smog reaction. It also reflected the greater progress which had been made in developing control devices for exhaust hydrocarbon from motor vehicles.

The Department did not include oxides of nitrogen in its motor vehicle emission standards in 1959. It concluded from the data then available that a large reduction in hydrocarbons would produce a marked improvement in smog effects and that there was insufficient evidence to support a standard for nitrogen oxides emissions.⁽¹⁾ At the present time no regulations specifically requiring nitrogen oxides control are in effect for either stationary or moving sources in the State of California.

Recently, intensified attention has been directed to the possible need for the control of oxides of nitrogen. The difficulty and expense of applying hydrocarbon controls to used vehicles has increased interest in the possibility of reducing photochemical smog by also requiring control of nitrogen oxides. Some individuals have expressed concern that, with the control of hydrocarbons alone, nitrogen dioxide atmospheric concentrations will increase because of incomplete reaction. The attendant color and toxic effects would then become a matter of greater concern.

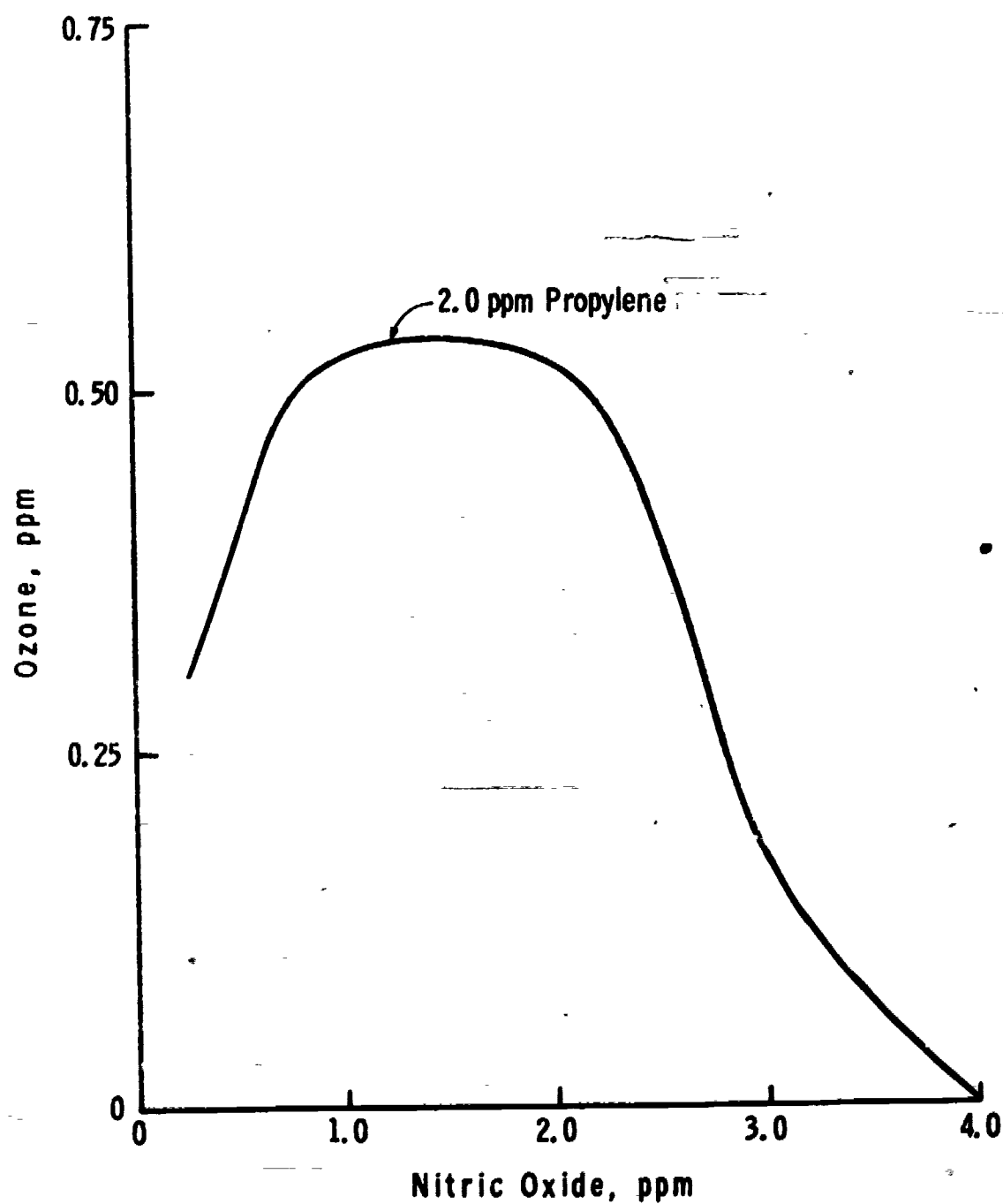
Experimental studies of the photochemical smog system have shown that the change in many smog effects which would result from an increase or decrease in nitrogen oxides concentration is dependent upon the hydrocarbon concentration. The converse is also true, although the change is not so prominent. For example, at any given hydrocarbon level, the peak ozone concentration can be reduced by either a large decrease in nitrogen oxides or by a large increase. This somewhat paradoxical situation underlies the difficulty in predicting the result of varying degrees of nitrogen oxides control on the photochemical smog effects. These effects bear no simple relationship to the concentrations of the primary reactants, but are complex functions of both the concentration and ratio of the reactants.

An example of this is shown in Figure 1. In this figure the maximum concentration of ozone developed in an experimental irradiation system is plotted against the initial concentration of nitric oxide. The propylene concentration is held constant for this series of experiments. It can be seen that, at first, the ozone increases directly with increasing oxides of nitrogen. At about 1.2 ppm of nitrogen oxides, the maximum amount of ozone is generated and further increases in nitrogen oxides result in progressive decreases in the maximum ozone concentration. While this curve is for a hydrocarbon concentration slightly higher than found in the atmosphere, it demonstrates that the photochemical smog system can provide exceptions to the "common sense" concept that the effects of air pollution are always decreased by the reduction in emissions of air pollutants involved.

The technical problems of developing and implementing control measures for either hydrocarbons or nitrogen oxides on upwards of ten million motor vehicles in California preclude any rapid or inexpensive solution. If controls are applied only to new cars, over a decade will be required to displace most of the uncontrolled vehicles and thereby realize the benefits of the control measures on the ambient air quality. This makes it necessary to consider not only the result of the final control levels on smog, but also the result of various intermediate degrees of control of both nitrogen oxides and hydrocarbons.

In the following pages it is assumed that control of hydrocarbon emissions from motor vehicles will be accomplished over a period of years. The result of supplemental control of nitrogen oxides on each of the following smog effects is postulated:

VARIATION OF MAXIMUM OZONE CONCENTRATION
WITH NITRIC OXIDE CONCENTRATION



SOURCE: DATA FROM IRRADIATION EXPERIMENTS IN STATE OF CALIFORNIA
DEPARTMENT OF PUBLIC HEALTH LABORATORY, 1964

FIGURE 1

1. Ozone formation in the atmosphere.
2. Eye irritation, including the formation of presently identified eye irritants (formaldehyde and peroxyacetyl nitrate).
3. Visibility reduction.
4. Vegetation damage.
5. Nitrogen dioxide formation in the atmosphere.

DISCUSSION OF PHOTOCHEMICAL REACTIONS

Photochemical air pollution is caused by the atmospheric reaction of organic substances and nitrogen dioxide under the influence of sunlight. A major role of nitrogen dioxide is to absorb the energy from sunlight that is required for the reaction to proceed.

In the absence of organic matter, the nitrogen dioxide provides a photochemical mechanism to convert solar energy to heat energy with little smog-forming consequence, the important reactions being:

1. $\text{NO}_2 + \text{ultraviolet light} = \text{NO} + \text{O}$
2. $\text{O} + \text{O}_2 + \text{collision body} = \text{O}_3 + \text{collision body} + 24 \text{ kcal}$
3. $\text{O}_3 + \text{NO} = \text{O}_2 + \text{NO}_2 + 48 \text{ kcal}$

The presence of reactive organic compounds greatly alters the balance of the above reactions while introducing many new reactions. Under these conditions nitric oxide, the principal state in which nitrogen oxides are discharged into the atmosphere, is converted to nitrogen dioxide and complex reactions take place between oxygen atoms, ozone, organic compounds, and nitrogen dioxide. Ozone and other products accumulate in the system and the typical photochemical smog effects are produced.

During a typical smog day the unreacted pollutants, hydrocarbons, and oxides of nitrogen, are usually at a maximum by 8:00 a.m. because of peak emissions from motor vehicles and because of meteorological conditions that restrict dilution. With increased sunlight intensity, the reaction begins. Hydrocarbons are consumed and nitric oxide disappears with attendant and parallel appearance of nitrogen dioxide. The nitrogen dioxide reaches a maximum and then decreases with the concurrent development of ozone. It is noteworthy that nitric oxide and ozone co-exist only at very low concentrations in the atmosphere. The development of ozone, therefore, attests to the nearly complete conversion of nitric oxide to nitrogen dioxide. Figure 2 shows these typical events. The oxidant trace shown is largely an index of ozone concentration.

DIURNAL VARIATION
 HOURLY AVERAGE CONCENTRATION FOR EACH HOUR
 FOR FIVE CONTAMINANTS
 DOWNTOWN LOS ANGELES - SEPTEMBER 3, 1964

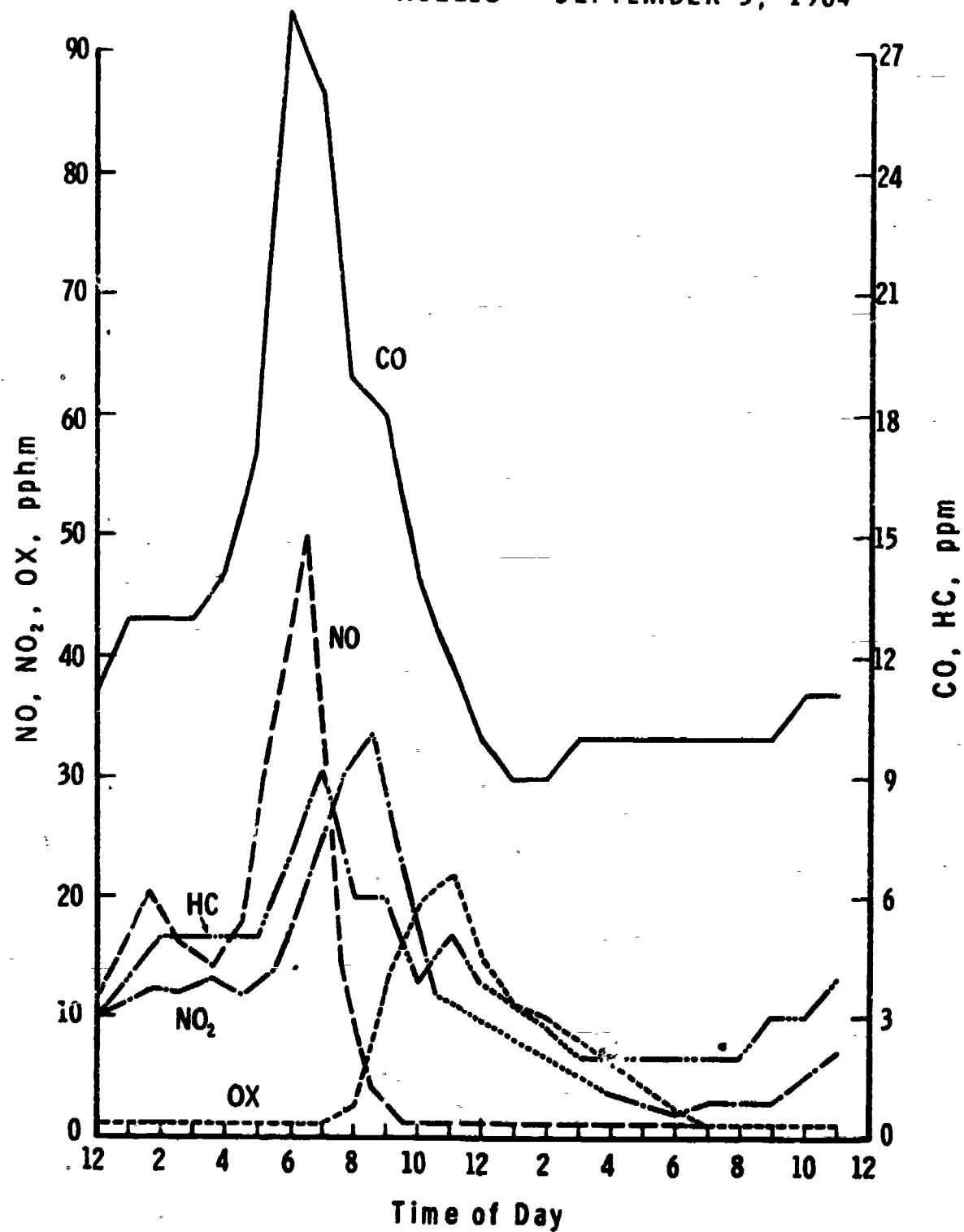


FIGURE 2

Some of the products formed during the course of the reaction have been identified. One important product, ozone, has already been mentioned. Others include peroxyacyl nitrates, formaldehyde, acrolein, and other oxygenated compounds. Well known effects of the photochemical reactions include irritation to the eyes and respiratory system, reduced visibility, and damage to vegetation.

INTERPRETATION OF LABORATORY FINDINGS

Most of the information on the photochemical smog reactions has been obtained from laboratory experiments. Such experiments were conducted with various controlled concentrations and ratios of hydrocarbons and nitric oxide to simulate the effect of different degrees of control of either reactant. The State Department of Public Health studies have made use of two 1000 cu. ft. irradiation chambers. In these large chambers, as well as in those of other agencies, reactions have occurred and effects have been produced which closely parallel the outdoor smoggy atmosphere. Nevertheless, a direct extrapolation of the test chamber data to the effects found in the atmosphere presents many difficulties.

One of the effects most difficult to extrapolate from irradiation chambers to the atmosphere is eye irritation. In the absence of definitive cause and effect relationships between the reaction products and the eye irritation effects, subjective responses of human subjects are utilized for laboratory evaluations. The different exposure situations, reaction conditions, and psychological influences require that somewhat higher contaminant levels be employed in the chamber to produce measurable effects than appear to be necessary in the atmosphere. Another difficulty resides in the selection of test panels which are representative of the general population. There may be some uncertainty in extrapolating effects from one concentration level to another for a system which is complicated by many competing reactions.

Problems also pertain to extrapolation of visibility findings. The visibility reduction cannot be observed in the laboratory under conditions simulating the ambient atmosphere and the effect must be assessed by physical or optical measurements of the contributing aerosols. The aerosols exist in different sizes, and interpretation involves correlations between reduced visibility and aerosol size and number. Laboratory studies on reduced visibility are also complicated by the role of an important third variable, sulfur dioxide. The role of sulfur dioxide has not been clearly established, but some experiments have shown this compound to be a factor in aerosol production.

Other difficulties arise in relating laboratory experiments to the atmosphere because the atmosphere is a changing system influenced by emissions from many sources, changing sunlight intensity, and variable temperatures. Wind and inversion conditions cause changes in the concentrations of pollutants from day to day and even from hour to hour. Many

of the laboratory studies were performed under static conditions where predetermined concentrations of reactants are irradiated at constant light intensity. Once the experiment starts, reactants are neither added nor removed from the system. Dynamic laboratory experiments also have limitations. Here the reactants are carried in an air stream which displaces the chamber contents at a fixed rate. Natural conditions are somewhat different from those prevailing in either the static or dynamic studies.

An important factor in interpretation of all chamber studies is the difficulty in eliminating inadvertent contamination of the chamber air so that the measured effects are due solely to the reactant charges. This is particularly difficult at realistically low reactant concentrations, where effects developed during blank runs may be as pronounced as those developed during tests with added reactants.

LABORATORY STUDIES

The first laboratory studies which led to the present understanding of photochemical smog were performed by A. J. Haagen-Smit⁽²⁾ in association with the Los Angeles County Air Pollution Control District. His early findings have been confirmed and extended through further studies by a number of other investigators representing the laboratories of Stanford Research Institute, Franklin Institute, General Motors Corporation, U.S. Public Health Service, Los Angeles County Air Pollution Control District, U.S. Bureau of Mines, University of California, and California Department of Public Health. The various studies have not always been strictly comparable either in facilities and experimental design used to simulate the atmospheric photochemical reaction or in the procedures used to characterize the smog produced. Hence, these studies have produced results that agree in many areas but disagree in others. Conclusions drawn from these investigations concerning control of photochemical air pollution, therefore, are not always identical. As a result, scientists have made different interpretations of the experimental data relating to the need for nitrogen oxides control. The extremes of opinion range from the assertion that nitrogen oxides control is necessary to reduce smog effects to the claim that control of nitrogen oxides is likely to make smog worse at a given hydrocarbon concentration.

The following conclusions are generally accepted by all investigators:

1. Both hydrocarbons and nitrogen oxides are essential to the photochemical smog reaction.
2. Highly effective control of either or both contaminants will be effective in reducing all manifestations of photochemical smog.

3. The magnitude of many smog effects as produced in laboratory experiments is not directly proportional to the concentrations of either hydrocarbons or nitrogen oxides considered separately. For a specific level of either contaminant there is a limited range of concentrations over which the other may vary and still produce maximum effect. Depending upon the relative concentrations of organics and nitrogen oxides, one or the other can exhibit an inhibitory effect on the progress of the reactions and the product yields. The inhibitory effect of excess hydrocarbons, however, is not as marked as that of nitric oxide.
4. Controlling oxides of nitrogen is effective in reducing the peak nitrogen dioxide concentration and its persistence in the atmosphere.

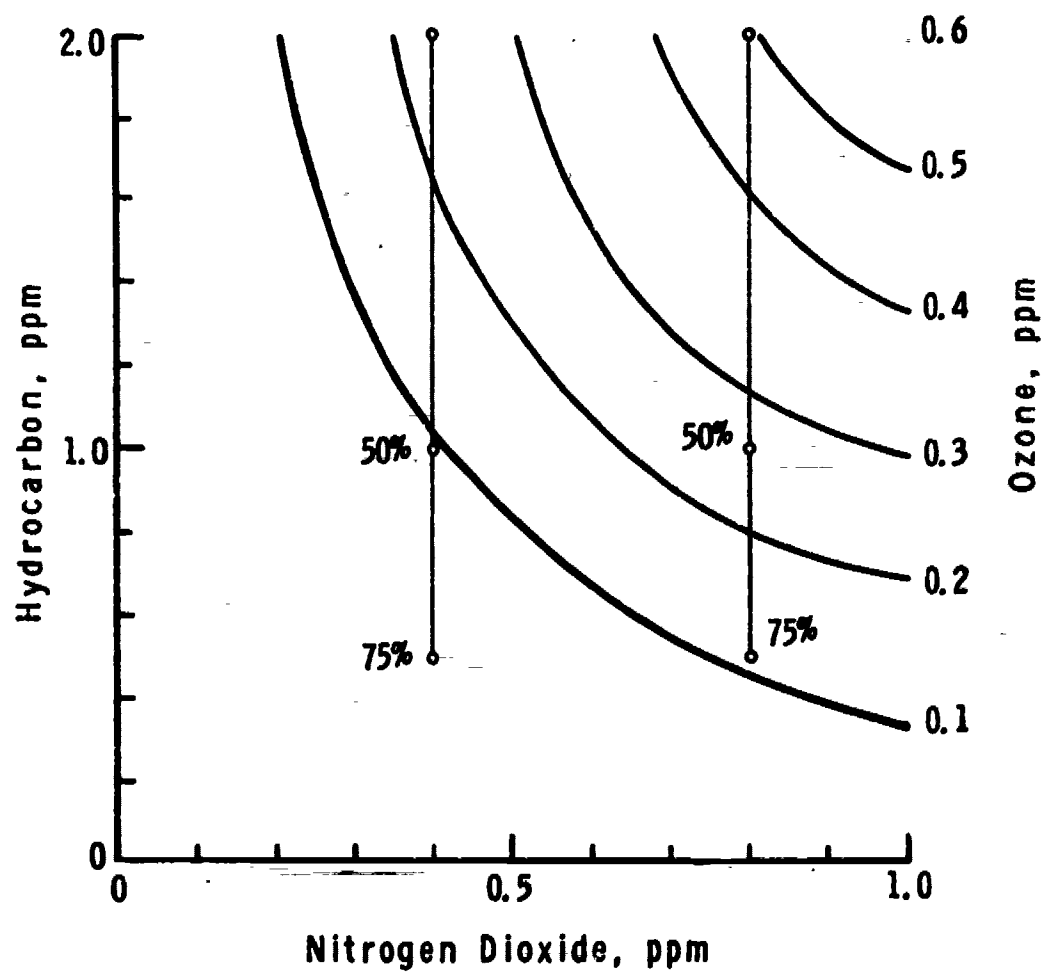
In some specific areas, findings and conclusions of some of the important investigations appear to contradict those of others. Examples of these findings and conclusions are summarized in the following paragraphs:

The appearance of eye irritation has been related to the arithmetic product of the concentration of hydrocarbons and nitrogen oxides.⁽³⁾ This relationship is illustrated for ozone formation in Figure 3, taken from an early paper presented by Haagen-Smit and Fox.⁽⁴⁾ This model of the system leads to the prediction that the benefits of control of both components are additive and that control of either at any level will result in improvement in the smog effects. At realistic atmospheric concentrations of reactants the model illustrated in Figure 3 has been applied to eye irritation as well as to ozone formation. The inhibitory effect of excess of reactants was observed by Dr. Haagen-Smit, but only at reactant concentrations somewhat above ambient levels.

Based on analyses of results from several experiments, it has been concluded⁽⁵⁾ that the contaminant ratio effect is indeed important at atmospheric levels; that moderate hydrocarbon control will result in increased eye irritation before further control begins to be beneficial; and that a noticeable reduction in eye irritation effects can be achieved earlier and maintained longer by first controlling the oxides of nitrogen. These conclusions are based in part on the interpretation of results obtained in a study employing auto exhaust performed by the Los Angeles County Air Pollution Control District under contract to the California Department of Public Health, and in part on the interpretation of other studies by that District, the U.S. Public Health Service, and Stanford Research Institute.

The conclusions listed above have not been confirmed by statistical analyses of the same data using a computer.⁽⁶⁾ From one set of analyses using computer techniques, it was concluded that there was little support in the data (those discussed in the previous paragraph) for action that might interfere with implementation of hydrocarbon control as it is now proceeding in the State of California. It was found also

OZONE FORMATION WITH
3-METHYLHEPTANE AND NO₂



SOURCE: REFERENCE 4

FIGURE 3

that the postulate of contours similar to those shown in Figure 3 did not describe results from chamber studies.

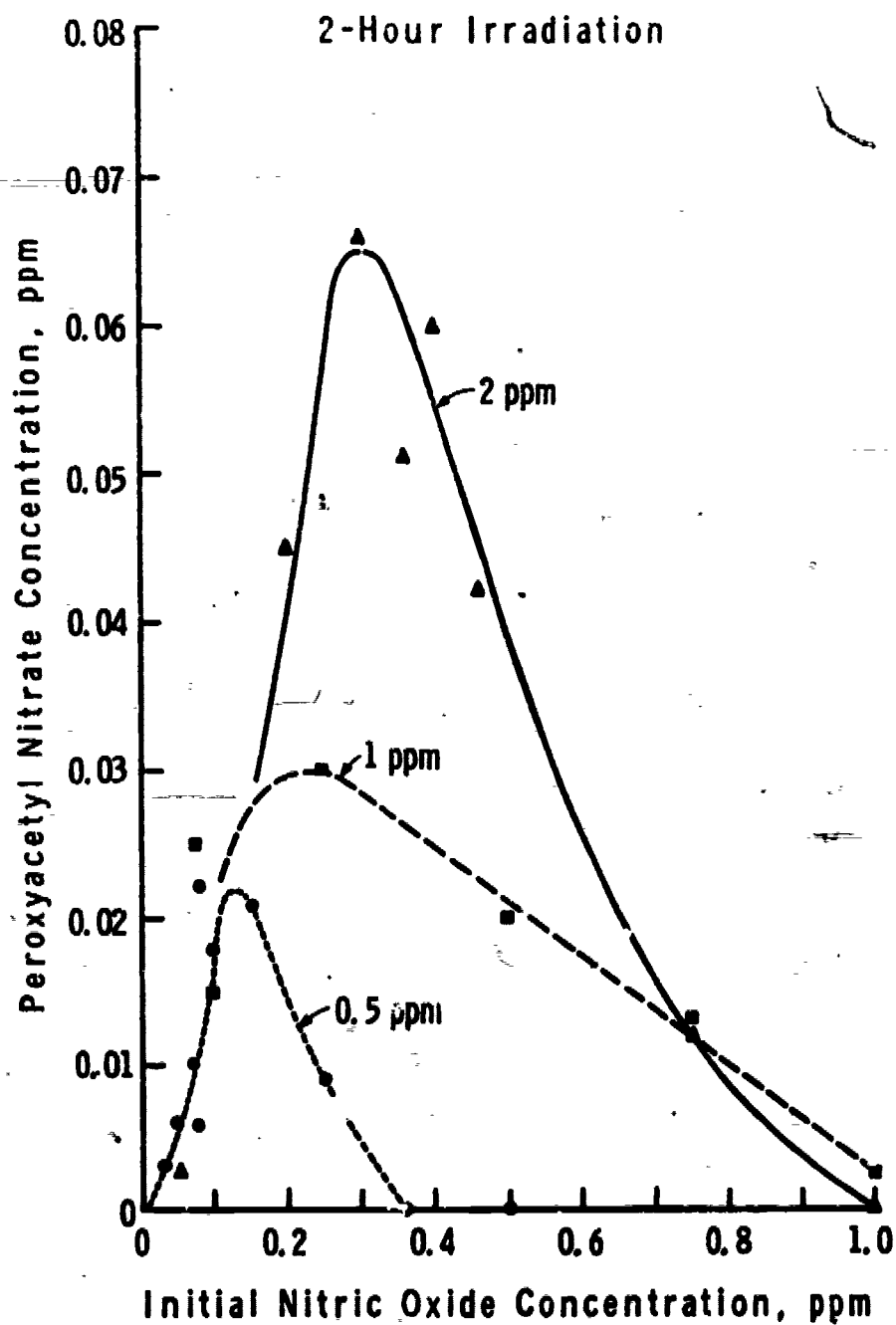
The State Department of Public Health has also made a computer analysis of the data produced in the contract study by the Los Angeles County Air Pollution Control District. The same general trends were obtained as by the District in the eye irritation response to hydrocarbon and nitric oxide control. However, the multiple correlation coefficient was only 0.67, indicating that results are not highly significant and should be used with caution for predicting absolute effects of given levels of control. The ozone and formaldehyde yields as joint functions of hydrocarbon and nitrogen oxides concentrations were only slightly more significant - multiple correlation coefficients of 0.72 in both instances. A multiple correlation coefficient of 0.99 was obtained, however, for the nitrogen dioxide time-concentration data. These data indicate that the control of nitric oxide would be a more effective way of decreasing nitrogen dioxide exposure than would be control of hydrocarbons.

The U.S. Public Health Service⁽⁷⁾ has studied contaminant concentrations that simulated 75 percent control of both hydrocarbons and nitric oxide in auto exhaust. Their results indicate that any degree of hydrocarbon control would cause a reduction in eye irritation, formaldehyde, ozone, and plant damage. At high nitric oxide levels, moderate hydrocarbon control would cause increased time-concentrations of nitrogen dioxide. The nitrogen oxides level for maximum eye irritation was about 1 ppm for all hydrocarbon levels. (Decreases from 1 ppm of nitrogen oxides showed less eye irritation.) Similar decreases, however, were not observed for formaldehyde concentrations. Also, 75 percent control of nitric oxide at any hydrocarbon level increased the ozone concentration. The inhibitory effect of nitric oxide was also evident in the plant damage phenomenon. As the nitric oxide concentration reached the hydrocarbon concentration, plant damage disappeared. Any degree of nitric oxide control was found to be effective in reducing the time-concentration of nitrogen dioxide.

In a study of hydrocarbon control on the plant damaging properties of irradiated auto exhaust from an automobile equipped with an afterburner, it was concluded that control of hydrocarbon alone would reduce eye irritation, but that nitrogen dioxide and perhaps other intermediate reaction products produced a new type of plant damage.⁽⁸⁾

The inhibitory effect of excess nitric oxide on a number of chemical manifestations of the photochemical system, including hydrocarbon reaction rates, ozone formation rate, and peroxyacetyl nitrate concentration, was demonstrated in the studies of Glasson and Tuesday.⁽⁹⁾ An example of their findings is shown in Figure 4. As the hydrocarbon concentration is lowered, the oxides of nitrogen concentration at which maximum manifestation occurs is also lowered. These findings and a review of published data appear to be the bases for the statement

PEROXYACETYL NITRATE FROM PROPYLENE PHOTOOXIDATION



SOURCE: REFERENCE 9

FIGURE 4

"Existing experimental evidence not only fails to support this assumption (that nitrogen oxides control will reduce smog effects) but strongly suggests that the reduction in oxides of nitrogen contemplated will increase rather than decrease both smog incidence and intensity." This statement was in the testimony given by a representative of the Automobile Manufacturers Association at a public hearing of the California Department of Public Health on a proposal for oxides of nitrogen control.

The California Department of Public Health has conducted chamber irradiation studies to determine the need for oxides of nitrogen and hydrocarbon control. In studies of propylene-nitric oxide mixtures, eye irritation was found to be significantly dependent only on the hydrocarbon level. An optimum hydrocarbon-nitric oxide ratio was suggested, but the relationship between this ratio and eye irritation was not firmly established. Formaldehyde production and hydrocarbon reaction rates were found to be significantly dependent only on hydrocarbon levels. The formaldehyde results are illustrated in Figure 5. Ozone yield was dependent on both nitric oxide and hydrocarbon with strong evidence of an optimum ratio.

Depending upon the initial levels of propylene and oxides of nitrogen, the control of either could result in an increase or a decrease in the ozone yield. The hydrocarbon-nitric oxide ratio for optimum yield was in the vicinity of 2.5 to 1 but was not sharply defined. There was some indication that the optimum ratio decreases as the hydrocarbon levels are lowered. Nitrogen dioxide time-concentrations were inversely proportional to the hydrocarbon level and directly proportional to the nitric oxide level. No evidence of dependence on an optimum ratio was apparent.

The U.S. Public Health Service is investigating the propylene-nitric oxide system in the same concentration ranges employed in the California Department of Public Health study. The experiments are being conducted under both static and dynamic irradiation chamber conditions and their preliminary results have been communicated privately.⁽¹⁰⁾

Although some differences exist between the U.S. Public Health Service and the California Department of Public Health propylene-nitric oxide study results, in general the two studies agree reasonably well. Both studies would seem to indicate that a substantial reduction in nitrogen oxide would be needed to obtain additional improvement in effects from photochemical air pollution, beyond that produced by a large reduction of hydrocarbons alone.

PREDICTION OF EFFECTS OF NO_x CONTROL

A review of the conclusion of the various investigators shows that the understanding of the mechanism of the photochemical reaction is not sufficiently precise to compel universal agreement on the benefits to

FORMALDEHYDE FROM PROPYLENE PHOTOOXIDATION

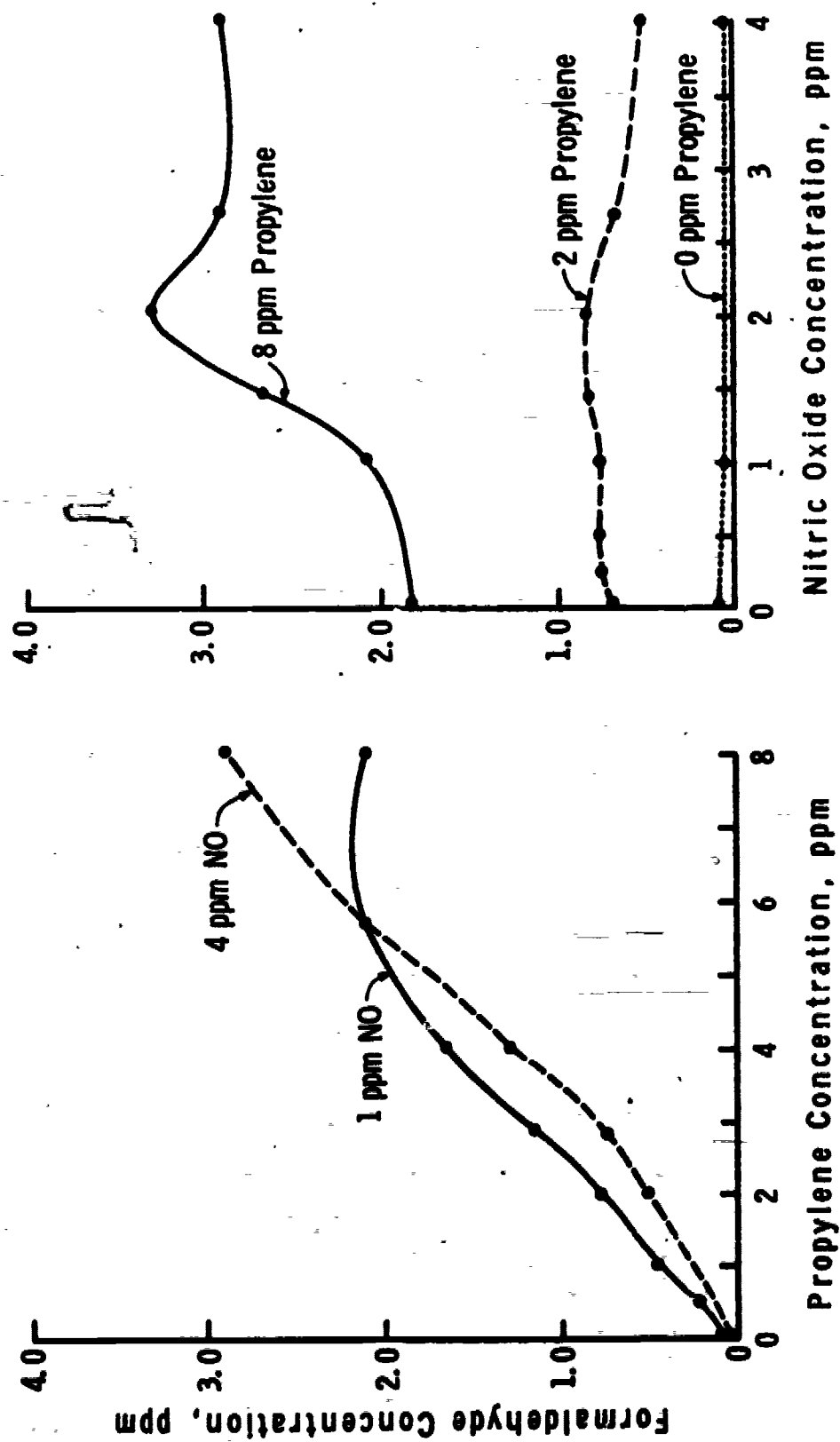


FIGURE 5

... expected from nitric oxide control. A consistent theme, however, runs through all of the studies which permits predictions of some effects.

At a given hydrocarbon level, the severity of smog first increases and then decreases as nitric oxide concentration is increased above zero. The nitric oxide concentration which produces the most severe smog increases with hydrocarbon concentration. The converse of this statement is also true but the point of inflexion takes longer to reach as the hydrocarbon concentration increases; the inhibitory effect of excessive hydrocarbon is not as marked as that of nitric oxide.

Although the result of a given degree of control in the atmosphere cannot be conclusively demonstrated, the effect of nitrogen oxides control on each of the known smog effects is postulated as follows.

OZONE

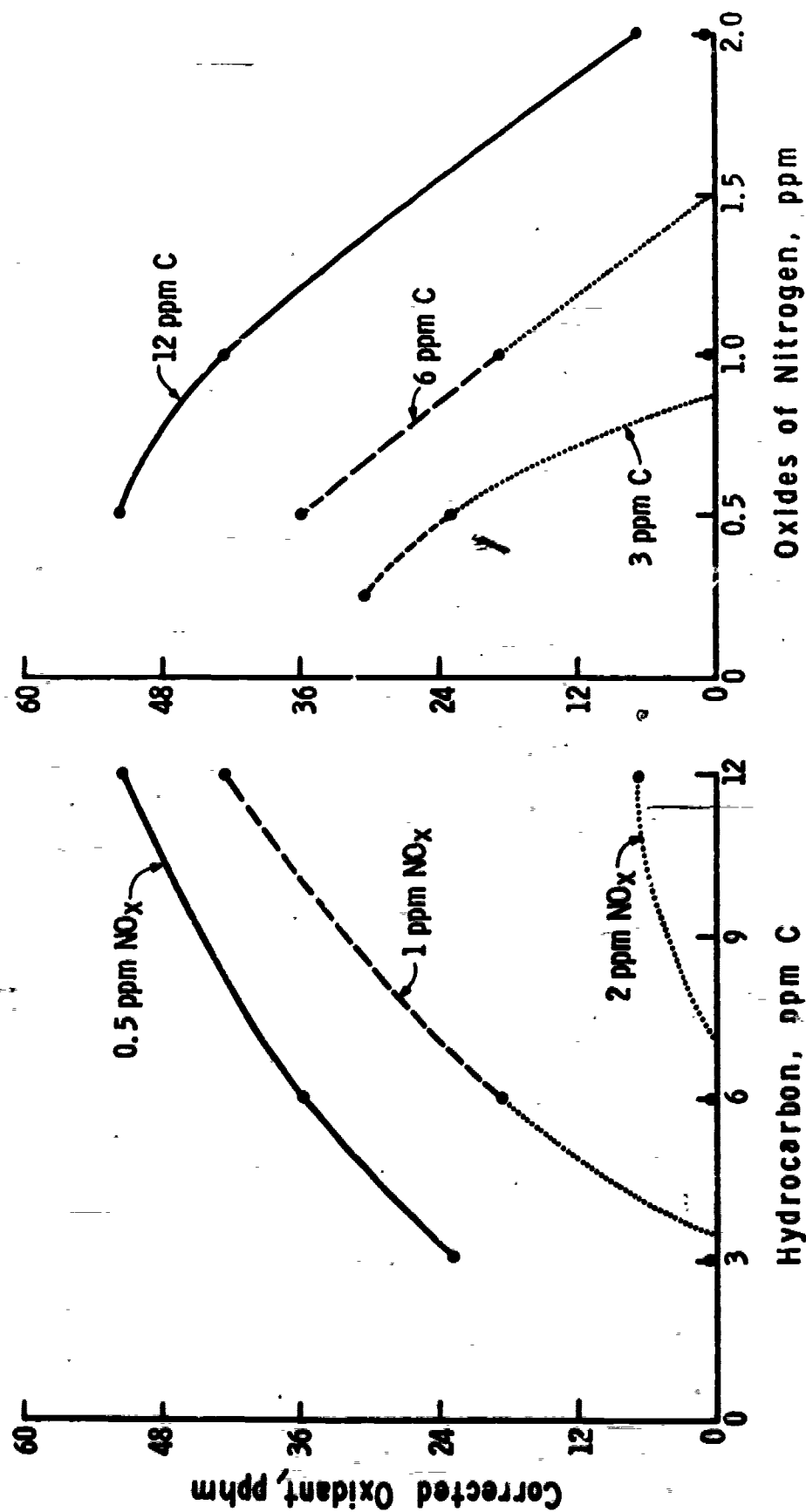
The inhibitory properties of both nitric oxide and hydrocarbon are readily apparent in the ozone parameter. The inhibitory effect of excess nitric oxide is more striking than that of excess hydrocarbons.

Maximum ozone concentrations are plotted as functions of hydrocarbon concentration and nitric oxide concentration for two important studies in Figures 6 and 7. The series shown in Figure 6, performed in a dynamic irradiation system, indicates that reduction of nitric oxide down to 0.25 ppm would result in increased ozone concentration. The series shown in Figure 7, run under static conditions, indicates that ozone levels would be reduced by nitric oxide control, at least when hydrocarbon levels are fairly high.

It is apparent that these two studies yield contradictory conclusions on the trend of oxidant concentrations with decreasing nitric oxide concentrations. Most other studies show that decreasing nitric oxide to some optimum ratio results in increased ozone (see Figure 1). Further decreases in nitric oxide result in a corresponding decrease in ozone. The optimum hydrocarbon-nitric oxide ratio varied widely for the different experimental systems that have been employed.

A substantial reduction in hydrocarbon levels will result in lower ozone concentrations. Following substantial hydrocarbon control, however, it is possible that reducing nitric oxide will negate some of the benefits of hydrocarbon control until a high degree of nitric oxide control is achieved.

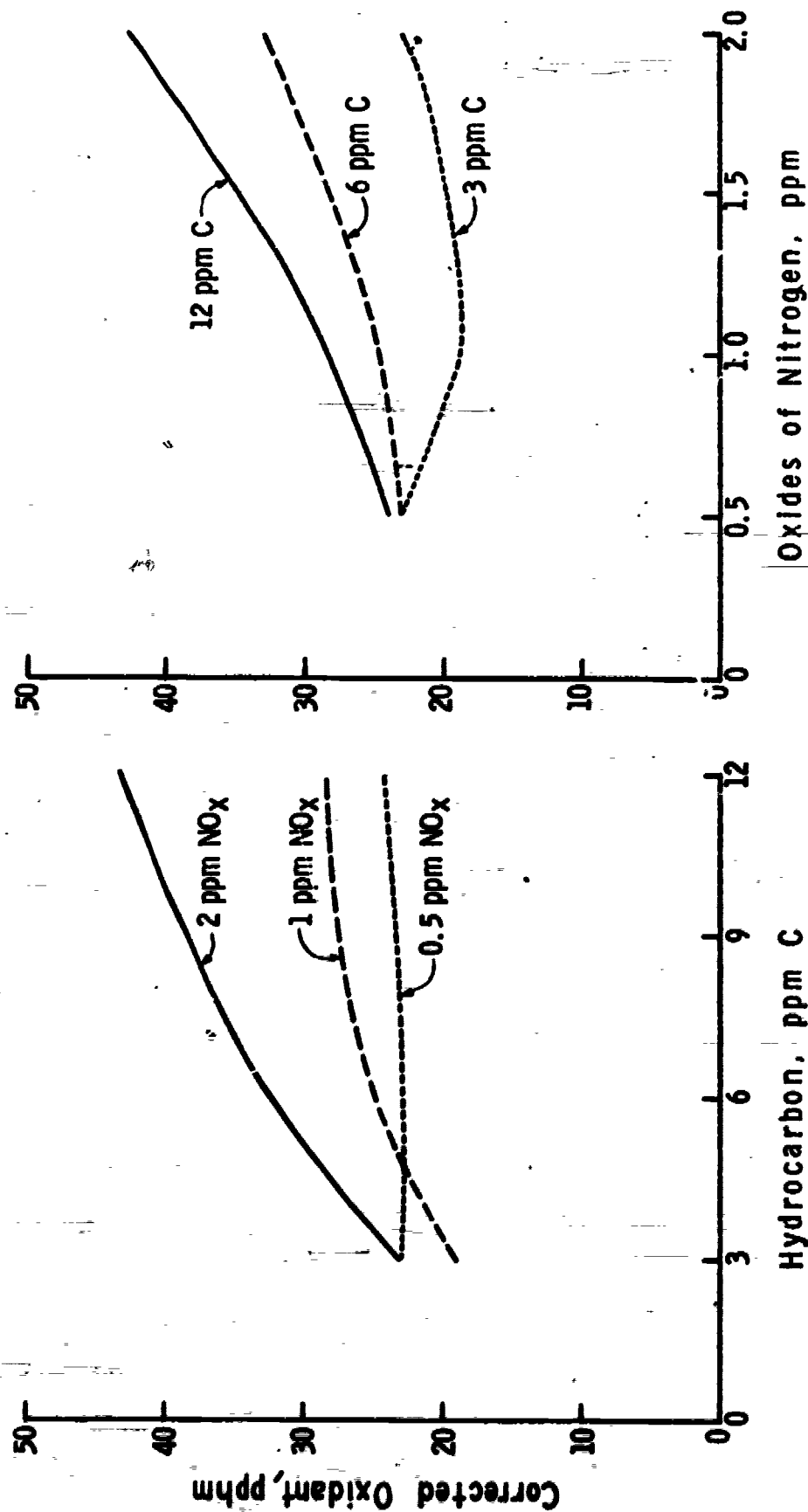
EFFECTS OF HYDROCARBON AND NITROGEN OXIDES ON PEAK OZONE (CORRECTED OXIDANT)



SOURCE: USPHS AUTO EXHAUST STUDY (REFERENCE 7)

FIGURE 6

EFFECTS OF HYDROCARBON AND NITROGEN OXIDES ON PEAK OZONE (CORRECTED OXIDANT)



SOURCE: LAAPCD-CSDPH AUTO EXHAUST STUDY, 1963

FIGURE 7

EYE IRRITATION

The variation of eye irritation with nitrogen oxides concentrations has been studied in the range of ambient air concentrations in two experimental series.⁽⁵⁾⁽⁷⁾ Both studies show an optimum nitric oxide concentration for maximum eye irritation and indicate that progressive reductions of nitrogen oxides below the level of 1 ppm will result in less eye irritation. The levels of eye irritation at the lowest hydrocarbon levels in these experiments were very near the blank level so the optimum ratio is not precisely defined. Furthermore, the results are not fully in accord with chemical measurements of known eye irritants made in the same and other experiments.

In the chemical measurements⁽¹²⁾ accompanying one of these series,⁽⁷⁾ neither formaldehyde (a known eye irritant) nor total aldehydes show a tendency to decrease markedly at low nitrogen oxides/hydrocarbon ratios. Later measurements made under similar conditions⁽¹⁰⁾ show that the nitrogen oxides level must be reduced to a low value before appreciable reduction in formaldehyde production occurs. In another experiment, the production of a known eye irritant - acrolein - has been shown to be unaffected by reduction of nitric oxide from 2 ppm to 0.5 ppm. When nitric oxide was further reduced to 0.1 ppm, the acrolein concentration was reduced only 50 percent.⁽¹³⁾

The appearance of these aldehydes in the photochemical smog system does not parallel that of ozone. Their formation parallels the disappearance of the hydrocarbons which occurs at a maximum rate shortly after the disappearance of nitric oxide. The concentration of aldehydes is relatively insensitive to changes in nitric oxide concentration and little effect from anything but a major control of nitric oxide is expected. By the same token nitric oxide control is not expected to cause formation of more aldehydes. There is no evidence that excessive concentrations of hydrocarbons inhibit the formation of aldehydes.

The class of compounds known as peroxyacyl nitrates (PAN) has been reported to be important phytotoxicants and eye irritants. They are produced in low concentrations in the atmosphere. Investigations by Stephens⁽¹¹⁾ have demonstrated that the appearance of PAN parallels the appearance of ozone. Glasston and Tuesday⁽⁹⁾ have found that PAN varies with nitric oxide concentration in the same way that the corresponding rate of ozone formation does (see Figure 4).

It appears that some eye irritants are relatively insensitive to changes in nitric oxide concentration and that others may be strongly affected by variation in nitric oxide concentration, with pronounced dependence on ratio. The optimum ratio for atmospheric conditions cannot be defined from existing experimental data. It can be concluded that eye irritation will be reduced by controlling hydrocarbons alone. If a substantial control of hydrocarbons is achieved, it is

not clear that subsequent control of nitric oxide would further decrease eye irritation unless a very high degree of control is also accomplished.

VISIBILITY

There is little information relating to aerosol growth as a function of hydrocarbon and nitric oxide control. The involvement of sulfur dioxide as a third variable in the photochemical generation of aerosols complicates the problem of predicting the effects to be expected from nitric oxide control. Aerosol formation in smog parallels or follows that of ozone and PAN, and hydrocarbon control alone is expected to reduce aerosol formation. Additional benefit may not be derived from subsequent nitric oxide control until a high degree of control is reached.

VEGETATION DAMAGE

Photochemical air pollution damage was first recognized by Middleton et al⁽¹⁴⁾ in 1944. A comprehensive review of this type of damage was made by Middleton⁽¹⁵⁾ in 1961. Extensive work at the University of California at Riverside has shown that ozone and peroxyacetyl nitrate are major components which have phytotoxic potential.

The observation⁽⁷⁾ that plant damage does not occur under hydrocarbon-nitric oxide conditions, where the formation of ozone is completely inhibited, is consistent with these findings. It is assumed that the model for ozone and peroxyacetyl nitrate response to nitric oxide control as discussed in the sections on ozone and eye irritation is appropriate also to the question of vegetation damage.

NITROGEN DIOXIDE MAXIMUM AND TIME-CONCENTRATION LEVELS

Nitrogen dioxide in the atmosphere results from the photo-oxidation and thermal oxidation of the nitric oxide emitted to the atmosphere. The peak concentration of nitrogen dioxide, therefore, is primarily determined by the amount of nitric oxide emitted to the atmosphere. This simple relationship is complicated, however, by the relative importance of the photo- and thermal oxidation rates and by the chemical reactions involving nitrogen dioxide. The reactions which consume nitrogen dioxide may be divided into two classes according to the presence or absence of nitric oxide. While nitric oxide is present, only a small fraction of the nitrogen dioxide is consumed. Thus, in static chamber experiments, the nitrogen dioxide peak concentration approaches the initial nitric oxide level. Following the conversion of nitric oxide to nitrogen dioxide, other reactions become possible, ultimately consuming all of the nitrogen dioxide if sufficient organic material is present.

When dilution takes place during the photochemical reactions, as in the atmosphere, the rate of nitric oxide oxidation will affect the magnitude of the nitrogen dioxide peak. The faster the nitric oxide is converted to nitrogen dioxide, the less dilution occurs in the interim and the greater the agreement between initial nitric oxide level and peak nitrogen dioxide concentration. It is also conceivable that there is an optimum reaction rate at which maximum nitrogen dioxide will obtain in the atmosphere. As nitric oxide continues to be emitted to the atmosphere, provided dilution forces are weak, a longer period taken to develop the peak will incorporate more of the nitric oxide emissions to the atmosphere in that peak and it will be higher.

Although the nitrogen dioxide peak height is limited by the nitric oxide concentration, the photochemical rate of its formation is determined by the concentration of hydrocarbons and other organics in the atmosphere. Control of these ingredients will tend to slow the rate at which nitric oxide is converted to nitrogen dioxide, allowing the dilution forces of the atmosphere to take a greater toll of both the nitric oxide and nitrogen dioxide, thus reducing the nitrogen dioxide peak height. The complete elimination of organics will not prevent the thermal oxidation from proceeding, however, and although the rate of this reaction is relatively slow at low concentrations, it increases according to the square of the nitric oxide concentration. In sunlight, an equilibrium is established which limits the extent of the thermal conversion, but the complete absence of hydrocarbon is necessary for this effect to become significant. In spite of the mitigating effect of these other influences control of the magnitude of the nitrogen dioxide peak is most directly dependent upon control of nitric oxide emissions.

More important physiologically than the magnitude of the nitrogen dioxide peak is the nitrogen dioxide dosage - a function not only of concentration but also of time. Meteorological and photochemical factors which influence the rate at which the nitrogen dioxide peak is reached also regulate the rate at which it disappears. Since reducing the hydrocarbon concentration results in a reduction of these rates, moderate control of hydrocarbon is expected to result in an increased dosage of nitrogen dioxide.

Control of nitric oxide will not only decrease the magnitude of the nitrogen dioxide concentration but also its persistence in the atmosphere.

CONCLUSION

Precise quantitative predictions cannot be made about the changes in the photochemical smog effects that would result from various degrees of control of either hydrocarbons or nitrogen oxides from motor vehicles. Although the findings of studies are not always consistent,

the Department believes the following conclusions are a reasonable interpretation of the existing experimental data:

1. The control of hydrocarbons, even without nitrogen oxides control, will produce beneficial results with respect to the photochemical smog effects - eye irritation, ozone concentration, visibility reduction, and vegetation damage. The improvement achieved is expected to be approximately proportional to the degree of control achieved.
2. Assuming a successful hydrocarbon control program for motor vehicles, the following conclusions have been made:
 - a. The improvement trend in photochemical smog effects, with nitrogen oxides control, is not expected to be proportional to the degree of that control. Little improvement from nitrogen oxides control is expected until some critical concentration is reached, following which further reductions of nitrogen oxides will achieve a steep decline in the smog effects.
 - b. A high degree of nitrogen oxides control would result in additional improvement in photochemical smog effects caused by motor vehicles. A goal of about 0.1 ppm or less of nitrogen oxides in the atmosphere on days of minimum dilution would probably be needed to achieve this benefit.
3. The less the degree of hydrocarbon control accomplished, the sooner can benefits be expected from nitrogen oxides control. The critical level mentioned in conclusion 2a is progressively raised as less hydrocarbon control is achieved.
4. Nitrogen dioxide maxima and the time-concentration exposure to nitrogen dioxide can be expected to increase in the absence of nitrogen oxides control. With moderate hydrocarbon control, the time-concentration levels will increase at a greater than linear rate with respect to increased nitrogen oxides emissions.

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Chapter IX

BIOLOGIC EFFECTS OF NITROGEN DIOXIDE

Nitrogen dioxide, which is among the most toxic of the oxides of nitrogen, is an important component in the complex of chemicals producing photochemical smog. It does not occur in community air as an isolated contaminant. If its potential harmfulness is to be assessed it is essential to understand its specific biologic effects. This review is concerned with NO_2 as if it were the single toxicant polluting the air breathed by a community and what standards for community air would be appropriate with this assumption and current knowledge.

Standards for nitric oxide are not being considered at this time. Although nitric oxide has been shown to be one-fourth to one-fifth as toxic as nitrogen dioxide in rats (Gray et al, 1952), there have been no known demonstrable cases of human nitric oxide poisoning. Rats inhaling nitric oxide for as long as nine days, at concentrations of 10 ppm, failed to exceed a detectable level of hemoglobin-nitric oxide complex (Sancier et al, 1962). The electron spin resonance method for detecting such complexes would detect as little as one-tenth percent of the complex in whole blood. Decisions to set air quality standards for nitric oxide must await further evidence of toxicity of this gas.

REVIEW OF LITERATURE

Several reviews of the literature on nitrogen dioxide have been prepared in recent years, including those of Goldsmith (1962), the Public Health Service (1962), Buell (1965), and Stokinger (1965). It seems unnecessary, therefore, to resummize in this chapter all literature on the subject in either narrative or chronologic form. Instead, material has been tabulated in a fashion which permits systematic consideration of effects that might be expected from exposure to various concentrations shown in ascending order as in Table I. A list of references, in alphabetical order, is at the end of this chapter.

The proven effects of NO_2 on man and lower animals are confined almost entirely to the respiratory tract. With increasing dosage, acute effects are expressed as odor perception, nasal irritation, discomfort on breathing, acute respiratory distress, pulmonary edema, and death. Nitrogen dioxide's relatively low solubility, however, permits penetration into the lower respiratory tract. Delayed or chronic pulmonary changes may occur from high but sublethal concentrations and repeated or continuous exposures of sufficient magnitude.

EFFECTS ON MAN

Effects on man will be considered first. The odor of nitrogen dioxide is detectable at levels which could occur in atmospheric pollution; 1 to

Table I
EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION ppm	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
1.	0.05 (0.1 mg/m ³) (as nitrogen oxides)	U.S.S.R.: maximum allowable concentrations—average during 24 hours	Wenling Histar rats continuously exposed for 2, 4, 5 or 6 weeks. No weight loss, no lung changes. Equivocal mean blood esterase changes. (Elevated at 5 weeks, lowered at 6 weeks.) Questionable delay of litters. (Study complicated by insecticide spraying.)	Ryazanov (1962)	42
2.	0.15 (0.3 mg/m ³)	U.S.S.R.: maximum allowable concentrations—single exposure		Ryazanov (1962)	42
3.	0.15 to 0.5			Ripperton and Johnston (1959)	39
4.	0.2	Calculated limit for space travel	Continuous exposure 90 days. Rats (Sprague-Dawley)—3% mortality (no increase). Guinea pigs—0% mortality. Dogs—0% mortality. Rats, guinea pigs gained well; dogs, rabbits, gained slightly; monkeys lost weight slightly. No pathological changes (compare items 22, 35). Continuous exposure for 3, 6, 9 months. Mice subsequently challenged with Klebsiella pneumoniae at LD ₅₀ . After 3 months exposure, 92% died (control 54%); after 6 months exposure, 86% died (control 48%); after 9 months exposure, 70% died (control 54%). (Compare items 15, 19, 28, 30.)	Stekinger (1963)	47
5.	0.5	Submarine maximum for 90-day dive		Bureau of Ships, U.S. Navy Dept. (1962)	9
6.	0.5 (1 mg/m ³)			Siagel (1965)	45
7.	0.5			Ehrlich (1965)	16

Table I

EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION ppm	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
8.	0.5		One hour exposure of <i>Photobacterium fischerii</i> . No effect on flash luminescence.	Serdt and Mueller (1965)	44
9.	0.8		Continuous to Sprague-Dawley rats for 2 years. Dying of old age, no pathologic changes; mean respiratory rate 63 per minute compared with 49 per minute in controls. (See items 20, 36, 52.)	Freeman (1965)	13
10.	1.0		Intermittent--6 hours a day, 5 days a week for 18 months. <div style="display: inline-block; vertical-align: middle;"> No changes in weight, hematologic values, or serum alkaline phosphatase. In rabbits--O₂ consumption normal. </div>	Wagner, et al (1965)	53
11.	1.4 (0.057 mg/L)		Intermittent--2 hours daily for 15-17 weeks. Rabbits gained less than controls but gained after exposure ceased. Pathologic changes described in lungs. (Compare items 12, 17, 18.)	Mitina (1962)	33
12.	1.4 (0.057 mg/L) + 50% 1.75 ppm or (0.005 mg/L)		Intermittent--2 hours daily, 15-17 weeks. No effect on weight gain. (Compare items 11, 17, 18.)	Mitina (1962)	33
13.	1 to 3	Over threshold		Meyers and Rice (1961) and AIHA Toxicology Comm. (1964)	32
14.	2.0	Maximum allowable concentration for industry (U.S.S.R.) as of 1959		Elkins (1961)	17

Table 1

EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION ppm	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
15.	2.5		Single exposure--2 hours. Mice challenged subsequently with <i>Klebsiella pneumoniae</i> --negative. (Compare items 7, 19, 28, 38.)	Ehrlich (1963b) Purvis and Ehrlich (1963)	15 38
16.	2.6 (0.005 mg/L or less)	127 men who worked for 3-5 years in sulfuric acid plants and as etchers in print shops. Mul- tiple symptoms, signs and blood changes reported. (No methods, criteria or actual data given.)		Vigdortschik, et al (1937)	50
17.	2.8 (0.0057 mg/L)		Intermittent--Rabbits exposed 2 hours per day for 15 and 17 weeks, and ob- served for additional 5-7 weeks. Loss of weight (later regained), de- crease in red cell count and hemo- globin. Decrease serum albumin and increase in serum globulin. (See items 11, 12, 18.)	Mitina (1962)	33
18.	2.8 (0.0056 mg/L) SO ₂ 3.5 ppm (0.001 mg/L)		Intermittent--Rabbits exposed 2 hours per day for 15 and 17 weeks to com- bination. Slight weight loss (less than NO ₂ alone), temporary decrease in RBC, no change in Hb, no change in serum proteins. (SO ₂ alone caused slight reduction in weight and Hb.) (Compare items 11, 12, 17.)	Mitina (1962)	33
19.	3.5		Single exposure of mice for 2 hours with subsequent challenge with <i>Kleb- siella pneumoniae</i> , threshold of ef- fect with increased mortality in ex- posed animals compared with controls. (See items 7, 15, 28, 38.)	Ehrlich (1963b) Purvis and Ehrlich (1963)	15 38
20.	4		Continuous to Sprague-Dawley rats for 20 weeks. Sacrificed animals show beginning changes in bronchial epithelium. (See items 9, 36, 52.)	Freeman (1965)	12

Table I
EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION ppm	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
21.	3 to 4 (Source: red fuming nitric acid)		Intermittent--4 hours a day, 5 days a week for 4-6 months. Rats--negative. (One group had less pneumonia than control.) Mice--negative. Guinea pigs--negative. Based on two autopsies each month. (Compare item 34.)	Gray, et al (1954)	23
22.	4.4 (8.3 mg/m ³)		Continuous for 90 days. Rats--13% mortality. Rabbits--55% mortality. Dog--0% mortality. Monkey--0% mortality. (Compare items 6, 35.)	Siegel (1965)	45
23.	4.5		Continuous for 90 days. Monkeys--0 of 10 died. Rats (Sprague-Dawley)--9 of 50 died. Mice--13 of 100 died.	Thomas and Back (1965)	49
24.	5	Threshold limit value for occupational exposures (average for 8-hour day, 5 days per week).		American Conf. of Gov. Ind. Hygienists (1954) to date	2
25.	5	Exposure of one asthmatic and one pilocarpinized volunteer for 5 minutes--no effects noted.		Meyers and Hine (1961)	32
26.	5		Intermittent--5 hours a day, 5 days a week for 16 months. Dog (item 10), rabbit (item 8), guinea pig (item 31), rat (item 60), hamster (item 20), mice (item 39): No mortality, no consistent pathologic changes. No increase in rabbit oxygen consumption. Tumor acceleration in rats (not statistically significant). (Compare items 10, 49.)	Wagner, et al (1965)	52

Table I

EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION ppm	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
27.	5		Intermittent—4 hours a day, 5 days a week for 6 months; $\frac{1}{2}$ hours a day for 5 days a week for 6 months. Guinea pigs showed no plethysmographic evidence of increased expiratory resistance. Pathology negative except slight acute tracheal inflammation and desquamative pneumonitis. Lung tissue antibodies in serum after 2 months. (160 hours.)	Balehum, et al (1965)	4
28.	5		Single 2-hour exposure followed by challenging exposure to Klebsiella pneumoniae 1, 3, 6 or 27 hours. No increased mortality. (Compare items 15, 19, 38.)	Ehrlich (1963a, b) Purvis and Ehrlich (1963)	14, 15 38
29.	5 to 10		Intermittent—8 hours per day exposure of tissue cultures. Mouse fibroblasts, liver cells, hela cells survived 8 hours exposure but many died after a few days.	Pace, et al (1961)	35
30.	9.3		Predicted beginning of effects in dogs from single 8-hour exposure, based on data by Carson (see item 51).	Goldsmith (1962)	20
31.	10	60-minute emergency exposure level for occupational exposure		AIHA Toxicology Comm. (1954)	3
32.	10	Maximum permitted for one hour in submarine		Bureau of Ships, U.S. Navy Dept. (1962)	9
33.	10	Normal volunteer exposed for 60 minutes interpreted as not showing impairment of pulmonary function.		Mayers and Hine (1961)	32

Table I
EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION ppm	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
34.	0 to 14 (Source: red fuming nitric acid)		Intermittent--4 hours a day, 5 days a week for 2-5 weeks. Rats--Acute rhinitis and tracheitis, also pneumonia in those killed early. In those killed 8 weeks or more after exposure, inflammation subsided but there were localized areas of emphysema. Nons died. (Compare item 21.) Continuous for 90 days. Rats, 37% mortality; guinea pigs, 63%; rabbit, 17%; dog, 0%; monkey, 33%. Definite pathological changes in lungs. (See items 6, 22.)	Gray, et al (1952)	22
35.	11.7 (22 mg/m ³)		Continuous to rats up to 213 days. Some weight loss, respiratory rate increased. One of 9 died with minor pathological changes. (See items 9, 20, 52.)	Siegel (1965)	45
36.	12.5			Freeman and Haydon (1964)	19
37.	13	Eight volunteers; 3 of 8 had eye irritation; 7 of 8, nasal irritation; 4 of 8, pulmonary discomfort; 6 of 8, olfactory sensation; 2 of 8, CNS effects; all predominantly slight.		Meyers and Hine (1961)	32
38.	15		Single 2-hour exposure of mice caused pulmonary congestion. Challenge with <i>Klebsiella pneumoniae</i> 1, 3, 6 and 27 hours later resulted in greater mortality than in nonexposed controls. (Compare items 7, 15, 19, 28.)	Ehrlich (1963a, b)	14, 15
39.	15-25		Intermittent--Rabbits, rats and guinea pigs for 2 hours a day for 5 days. Nonfatal pulmonary edema, peribronchial and perivascular chronic inflammation, repair almost complete by 7th day postexposure.	Kleinerman and Wright (March 1961)	28

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EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION ppm	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
40.	15-20	/	Single exposures (2 hours) to rats and guinea pigs--mild pulmonary edema and inflammatory changes reversible.	Kleinerman and Wright (March 1961)	28
41.	15-20		Intermittent--10 guinea pigs, 2 hours a day, 3 times a week for 3 weeks, rest a week, 75-80 ppm for 2 hours, rest a week and repeat cycle once. After 14 days dilation of respiratory bronchioles and alveolar ducts, resembling centriolebular emphysema in humans.	Kleinerman and Wright (March 1961)	28
42.	20	Workers in HMC's recovery plants reportedly exposed to levels averaging up to 20 ppm for up to 18 months showed no ill effects.		Petty (1962)	36
43.	20	Emergency exposure limit for 30-minute exposure.		AIHA (1964)	3
44.	25	Emergency exposure level for 15-minute exposure.		AIHA (1964)	3
45.	25	Human volunteers exposed for 5 minutes. Slight or moderate nasal discomfort in 5 of 7, pulmonary discomfort in 3 of 7, odor detected by 6 of 7. No consistent changes in inspiratory reserve, expiratory reserve, vital capacity or MEC.		Mayers and Hine (1961)	32
46.	25		Single exposure of mice for 2 hours. No deaths, but lungs showed congestion and dilatation of veins and capillaries. (Compare item 47.)	Ehrlich (1963a, b)	14, 15

Table 1

EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION, PPM	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
47.	25 • bacteria		Single exposure of mice for 2 hours followed by <i>Klebsiella pneumoniae</i> at LD ₅₀ 1, 3, 6 and 27 hours later. All groups exposed to NO ₂ had higher mortality than controls. (Compare item 46.)	Enrich (1962a)	14
48.	25		Single exposure of rabbits for 2 hours. Moderate pulmonary edema at 24 hours, at 4 days replaced by macrophage infiltration and epithelial regeneration. At 2 weeks, repair nearly complete. (See item 4.)	Kleinsman and Wright (1961)	29
49.	25		Intermittent--5 hours a day, 5 days a week for 18 months. Rabbits (item 4), guinea pigs (item 15), rats (item 40) and hamsters (item 40). No change in body weight, hematologic findings, serum alkaline phosphatase. Oxygen consumption of rabbits showed slight transient elevation at end of week. (Compare items 10, 26.)	Wagner, et al (1965)	53
50.	25		Intermittent--Mice exposed 30 minutes a day, 5 days a week for 4½ months. Survived without symptoms. Pathology negative. (Controls for carbon studies.)	Boren (1964)	6
51.	25		Intermittent--4 hours a day for 30 exposures over 45 days. Zero of 10 guinea pigs and 0 of 10 rabbits died. When sacrificed, showed no diffuse fibrosis, focal emphysema, or bronchiolitis fibrosa oblitterans.	Hime, et al (1964)	27

Table I
EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION ppm	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
52.	25		Continuous exposure of rats up to 180 days. Eleven of 15 died; 3 of 15 sacrificed. Lungs showed hypertrophy and hyperplasia of bronchial and bronchiolar epithelium, increased goblet cells. Alveolar ducts and alveoli variable in size, many larger than in controls. Lungs voluminous. (Compare items 9, 20, 26.)	Freeman and Haydon (1964)	19
53.	25-38	Short exposures of workmen resulted in no demonstrable physiologic response.		Adley, F.E. (1946)	1
54.	28		Single 60 minutes to rats. Threshold for beginning toxic effects, based on lung-to-body weight ratio.	Cernon, et al (1962)	10
55.	30 (Source: copper + HNO_3)		Single exposures for 3 hours. Guinea pigs negative.	LaForsky, et al (1941)	30
56.	30-35	Workers exposed in 30-35 ppm of nitrous fumes over several years; had no ill effects.		Vigliani and Zurlo (1965)	51
57.	35-40 (68 mg/m ³)		Intermittent—8 hours a day, 5 days a week for 30 exposures (6 weeks). Four of 15 rats, 6 of 15 guinea pigs, 3 of 3 monkeys and 2 of 3 rabbits and 0 of 2 dogs died. Hemorrhagic pulmonary edema.	Siegel (1965)	45
58.	35	Emergency exposure level for 5 minutes.		ATHA (1964)	3
59.	50	Seven human volunteers exposed for one minute. Three had pulmonary discomfort and nasal irritation.		Mayers and Hine (1961)	32
60.	50		Single exposure of rats, mice, guinea pigs, rabbits and dogs for 1 to 24 hours. Three of 10 rats and 5 of 10 mice died at 24 hours.	Hine, et al (1964)	27

Table I
EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION ppm	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
61.	50-100	Described as causing bronchitis, little fibrosis obliterations and focal pneumonia with recovery in 6-8 weeks. No precise data given.		Grayson (1956)	25
62.	55		Single exposures 2-3 hours not lethal to rats, rabbits and guinea pigs; minor effects on mice and rats.	Leffowsky, et al (1941)	30
63.	50-75		Varying patterns of exposure resulted in fibrotic lesions in lungs of rats, mice and guinea pigs.	Hine, quoted by Goldsmith (1961)	20
64.	Over 50		Intermittent--5 hours daily for one month to rabbits, guinea pigs and pigeons, produced weight loss, decreased production of specific anti-toxins and decreased resistance to infectious diseases.	Ronzani (1908)	41
65.	60		Single exposure for 10 minutes caused cessation of ciliary activity in excised rabbit tracheas, without recovery.	Cralley (1942)	12
66.	64	Moderate irritation of larynx and increase in respiratory rate in volunteers.		Lehman and Hasagawa (1913)	31
67.	65		Threshold concentration for toxic effects of 15-minute exposure of rat, based on lung-to-body weight ratio.	Carson, et al (1961)	10
68.	65		Single exposure of 8 hours. Deaths in 7 of 15 rats, 13 of 15 guinea pigs, 3 of 3 monkeys, 1 of 3 rabbits and 2 of 2 dogs. Most deaths on first day with hemorrhagic pulmonary edema.	Siege! (1965)	45
69.	70		Acute exposures of 2BC mice sacrificed 2-100 days later, 40% showed bronchiolitis fibrosa obliterations.	Solomon, quoted by Buell (1965)	8

Table I

EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION ppm	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
70.	65-75		Acute exposures of dogs for 4 hours caused deaths.	Gray, et al (1959)	21
71.	80	In 3-5 minutes volunteers got tightness of chest.		Adley (1946)	1
72.	88		LC50 for acute exposure of rats for 4 hours.	Gray, et al (1954)	23
73.	75-85		Guinea pigs, exposed 2 hours every 2 weeks and 2 hours every week for up to 22 months, showed acute inflammatory and epithelial reactions which regressed after exposures stopped. No bronchiolitis obliterans, permanent fibrosis or emphysema.	Kleinerman and Wright (December 1961)	29
74.	100	Produced marked irritation of larynx and cough in volunteers.		Lehmann and Hasegawa (1913)	31
75.	100		Acute exposures above this level were lethal to rats, rabbits, guinea pigs, mice and rats in 10 minutes to 21 hours.	Leffowsky, et al (1941)	30
76.	100		Rabbits exposed for 2 hours a day died after exposures ranging 2 days to 40 weeks, with "degenerative lesions in lungs and acute pneumonia."	Robson, et al (1934)	40
77.	100		Continuous exposures of animals; rats--began to die in 24 hours with acute pulmonary edema and focal hemorrhages.	Freeman and Haydon (1964)	19
78.	100		Intermittent--2-hour exposure of rabbits once every 2 weeks or once every week for 15 months produced acute reactions which cleared after stopping exposure.	Kleinerman and Wright (December 1961)	29

Table I
EFFECTS OF NITROGEN DIOXIDE ON MAN AND LOWER ANIMALS

ITEM	CONCENTRATION ppm	MAN	LOWER ANIMALS	REFERENCE	
				Source	Number
79.	100		One-hour exposure fatal to rats; mice in 2 to 1 hour; guinea pigs and rabbits in less than 2 hours.	Hine, et al (1964)	21
80.	104		Threshold for toxic effect on rat for 5-minute exposure based on lung-to-body weight ratio.	Carson, et al (1962)	10
81.	110		Five-minute exposure of isolated tracheae of rabbits produced cessation of ciliary activity without recovery.	Cralliey (1942)	12
82.	115		LD ₅₀ for 60-minute exposure of rat.	Carson, et al (1962)	10
83.	150		Two hours to rats—all died within 24 hours.	Kleinerman and Wright (1961)	28,29
84.	162		LD ₅₀ for 30-minute exposure, rat.	Carson, et al (1962)	10
85.	166		LD ₅₀ for 60-minute exposure, rat.	Gray, et al (1964)	23
86.	174		LD ₅₀ for 30-minute exposure, rat.	Gray, et al (1964)	23
87.	200		Exposure for 5-10 minutes fatal to rats, mice, guinea pigs; 20 minutes fatal to rabbits and dogs.	Hine, et al (1964)	27
88.	201		LD ₅₀ for 15-minute exposure, rat.	Carson, et al (1962)	10
89.	250-500		LD ₅₀ for 30-minute exposure, mice.	Boren (1954)	6
90.	300-400	Few minutes' exposure will cause bronchopneumonia and death.		Grayson (1956)	25
91.	315		LD ₅₀ for 15-minute exposure, rabbit.	Carson, et al (1962)	10
92.	416		LD ₅₀ for 5-minute exposure, rat.	Carson, et al (1962)	10
93.	420		LD ₅₀ for 15-minute exposure, rat.	Gray, et al (1964)	23
94.	500	Few minutes' exposure will cause pulmonary edema.		Grayson (1956)	25

3 ppm (parts per million) has been demonstrated to be the threshold for this effect. Nasal irritation and eye irritation, however, do not usually occur until levels are reached well above those expected in atmospheric pollution. In one study, even at 13 ppm, only three out of eight volunteers complained of eye irritation, although seven out of eight had nasal irritation. Concentrations which have caused death from acute pulmonary edema in man have been poorly documented, but indirect evidence indicates they were in excess of 100 ppm. The concentrations which lead to delayed effects, such as bronchiolitic fibrosa obliterans, are also far too high for relevance to standards (Lowry & Schuman, 1956). There is little in the literature which verifies pulmonary effects in man other than transient discomfort at concentrations below 50 ppm. The single report suggesting such effects (Vigdortschik et al., 1937) cites not only emphysema but multiple symptoms, signs, and hematologic and biochemical changes in workers inhaling as little as 2.6 ppm for several years; however, the report does not contain any diagnostic criteria or data that would permit evaluation. Reports which indicate an absence of effects in individuals inhaling up to 20 ppm, or 30-35 ppm, are similarly lacking in data or assurances as to the actual concentrations of NO₂ encountered.

EFFECT ON ANIMALS

It is obvious that experimental and epidemiologic data on man are extremely limited in the low concentrations likely to be found in community air. At the present time, therefore, the biological basis for estimating levels at which effects may occur for NO₂ must depend on animal studies. Since the irritant qualities of the gas and the locus of action are the same, cautious application of these data to man is justified despite the quantitative differences known to exist in the responses of several animal species. Concentrations of NO₂ over 200 ppm are fatal to most species even after single brief exposure - for example 5 to 15 minutes. Concentrations between 100 and 200 ppm, continued for 30 to 60 minutes, were also fatal to most species, as were concentrations of 50 ppm or more continued up to 8 hours. Continuous exposures of 25 ppm were fatal to rats but intermittent exposures (6 hour/day) were not. Even concentrations below 5 ppm, if maintained continuously, have led to increased mortality in rats and mice; while intermittent exposures were not associated with deaths until concentrations reached 35 to 50 ppm. Two facts are obvious in reviewing the data on lethal effects. One is that high concentrations for short periods of time have a greater relative effect in terms of death or acute pulmonary damage than do lower concentrations over longer periods of time (Gray, 1959; Carson et al., 1962; Hine et al., 1964). The second is that intermittent exposures with intervening recovery periods are less harmful to experimental animals than continuous exposures. Of course, neither continuous nor intermittent exposures are directly comparable to the cyclic and variable exposures encountered in community air.

Summarization of the animal studies aimed at demonstrating subtle, chronic, or delayed effects resulting from continued or repeated exposures to low levels of NO₂ is complicated by the great variety of species, exposure patterns, and timing of observations. In general, exposures to between 10 and 20 ppm of NO₂ produces definite and persistent pathologic changes in the lungs. Between 5 and 10 ppm, results are equivocal, with animals continuously exposed sometimes exhibiting changes in bronchial epithelium; but intermittent exposures yielded negative findings. Balchum et al. have shown that exposure of guinea pigs to as little as 5 ppm produces⁽¹⁾ minor pulmonary changes and⁽²⁾ the development of circulating substances capable of agglutinating normal lung proteins.

Minor changes in the bronchial epithelium have also been described by Freeman and Haydon in rats exposed continuously to 4 ppm for 20 weeks. Although Mitina described distinct pathological changes in rabbits exposed to 2.8 ppm and 1.4 ppm intermittently for 15 to 17 weeks, other competent workers have not reported such changes in animals exposed to similar and higher concentrations. A toxic potential is confirmed by the demonstration by Buell (1965) on the ability of NO₂ to denature what was believed to be collagen and elastin in rabbit exposures in vivo, the increase in oxygen consumption of spleen and liver homogenates reported by Buckley and Balchum (1965), and the work of Pace showing effects on tissue cultures. It is impossible to translate these directly into standards at this time.

Since NO₂ is one of many toxicants present in community air, it is important that it remain at or below the lowest level at which one would predict a minimal effect on the health of the most susceptible individuals in the community. The most sensitive indicator so far discovered for a biologic effect of NO₂ is the production of increased susceptibility to infection by certain aerosolized bacteria. By this technique, Ehrlich and Purvis have demonstrated increased mortality in mice from Klebsiella pneumoniae (at approximately LD₅₀) following 2 hours of exposure to 3.5 ppm NO₂, and following 3 months' continuous exposure to 0.5 ppm NO₂. However, this was not found for all strains of mice and hamsters. Some required over 2 hours exposure at 25 to 30 ppm of NO₂. Translation of this effect to man and other infectious agents can be only speculative at this time. The experiments cited were deliberately designed to create the most sensitive possible indication. Care was taken not to introduce any direct effect of the gas upon the microorganisms which might reduce the effective dosage. Nevertheless, the work appears important in pointing toward possible interrelationships between air pollutants and altered responses to infectious disease. A changing and poorly defined group of susceptible individuals would be present in any community, representing those at the critical point of dosage and immunity to still unspecified infectious diseases. In this group a minor alteration in local defensive mechanisms might be critical in determining the course of an infection. The presence or absence of appropriate organisms might well determine the consequences in terms of pneumonia or

bronchiolitis which might follow a more severe exposure to an irritant gas such as NO₂. Thus, on the basis of this preliminary exploration and though the evidence is scanty, the exposure of large populations to continued concentrations of NO₂ exceeding 0.5 ppm could not be justified; nor could intermittent exposures above 3.5 ppm.

There is no evidence of any carcinogenic effects of NO₂ in man, and that animal experiments is not convincing. The data of Wagner et al (1955), in which the time of appearance of tumors in a tumor-susceptible strain of mice was questionably accelerated (although the total number over 18 months was not affected), involved too few animals to be statistically significant and cannot be regarded as proof of such activity unless repeated. The carcinogenic effect, therefore, does not appear relevant at this time to the setting of air quality standards.

The role of particulates which are always present in the atmosphere is worthy of special consideration. Boren has exposed mice to NO₂ adsorbed on carbon particles with resultant focal destructive lesions. This work, like the still unpublished work of Tyler using NO₂ on carbon particulates in horses, may alter present views in regard to acceptable concentrations of pollutants when there are concurrent particulates which may concentrate chemical action in vulnerable points of the lung. So far these techniques have not been applied in a manner permitting their quantitative interpretation for air quality standards. Boren used carbon with approximately 550 mg of NO₂ adsorbed per gram of carbon, of which 525 mg could be recovered by heating or negative pressure. It had been prepared by shaking carbon in a flask containing NO₂ until no more NO₂ was adsorbed. No long-term experiments have been carried out in which particulates have been introduced into exposure chambers during the exposure of animals at relatively low concentrations of NO₂; nor has there been any theoretical development of the predicted adsorption by carbon or other particles under such circumstances.

APPLICABILITY OF PRESENT DATA TO AIR QUALITY STANDARDS

A review of the toxicologic studies in lower animals makes it apparent that NO₂ when present for brief exposure periods can be tolerated at much higher concentrations than when there are continuous exposures with no opportunities for recovery. In atmospheric pollution, the concentration of NO₂ is characteristically cyclic and probably more closely resembles the intermittent experimental situation. Accepting the principle that an ambient air quality standard should be based on evidence of a beginning effect on the most susceptible individuals in the population, existing knowledge has been appraised for such an effect. The apparent augmentation of certain infections in animals is the most sensitive indicator so far noted, with detectable odor in man being the next most sensitive indicator.

Granting that evidence is still insufficient for a definitive judgment, it at least equals that existing for many other toxic substances in industrial toxicology and warrants considering tentative levels for atmospheric NO₂ for:

- a. Long-continued exposure.
- b. Brief and transient periods of exposure.

For long-continued exposures without periods of recovery, the average concentration should not exceed the range 0.5 to 1.0 ppm. These values are based primarily upon the evidence of increased mortality from aerosolized microorganisms after such exposures. Such a level for continuous exposure would provide a margin of safety against the effects, often fatal, encountered in continued exposures of lower animals at levels between 4 and 5 ppm.

For transient exposures, there is no evidence that any damage occurs at levels below 3.5 ppm, even with susceptible species and individuals. Accordingly, a level of 3 ppm is suggested as the maximum to be permitted for periods up to one hour. This is based upon (a) the evidence for augmentation of infection with exposures of 3.5 ppm, for 2 hours, with no positive effects at 2.5 ppm for the same period; and (b) the fact that this level is detectable as an odor by most individuals; and (c) it appears low enough even if repeated at irregular intervals over many months not to lead to pulmonary disease.

The above evaluation is made in full cognizance of the fact that other consideration, such as plant damage, visibility, or combined effects with other air pollutants, may be more critical than the health effects of nitrogen dioxide alone.

ACKNOWLEDGMENT

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